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ORGANIC BINDERS FOR IRON ORE PELLETIZATION

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 25 March, 2015.

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Abstract

Organic binders generally do not contain high quantities of silica and alumina and are burnt during pre-heating, contrary to bentonite clays commonly used in pelletizing iron ore for blast furnaces. Due to the need to process increasing volumes of low grade iron, interest in organic binders has increased lately. Organic binders tend to produce good quality wet pellets which however often lack in compressive strengths after sintering. The objective of this thesis is to determine what type of organic binders produce good quality pellets based on literature and testing different binders.

Carboxymethyl cellulose (CMC) and polymer binders with different viscosities and charge densities are tested to evaluate their effect on pellet quality. Two silanes were also tested as additives. To evaluate the pellet quality, size distribution, drop numbers, compressive strengths of wet, dry and sintered pellets, porosities and tumbling indices are determined.

According to tests the viscosity of 0.5 w-% solutions should be approximately 30 Cp for the binder to control the pelletizing process and achieve high portion of 10-12.7 mm target sized pellet. Significantly higher viscosities may cause problems distributing the binder evenly and hinder the pellet growth due to low surface moisture. For CMC binders the compressive strengths of dry pellets increased with increasing charge density, as expected from the literature, whereas the opposite was observed for the CMC binders. The difference between the different binders may be due to their structures: CMC structure is optimal with OH groups increasing the affinity of COO^- towards the iron oxide, whereas the polymers had only electron-withdrawing carboxyl acid and amide groups.

Due to their hydrophobicity silanes increased surface moisture of pellets resulting in larger amount of 10-12.7 mm pellets being produced. Aminosilane significantly increased only the drop number, while ureidosilane increased only the compressive strength of dry pellets. Thus the silanes tested are not viable additives for iron ore palletization. Aminosilanes were found to have a positive effect on plasticity of pellets and ureidosilanes for compressive strength of dry pellets. However, the overall performance of the tested silanes were not very good and they would not be considered as viable additives for iron ore palletization

Keywords organic binder, pelletizing, agglomeration, iron ore, iron oxide

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Tiivistelmä

Orgaaniset sideaineet eivät sisällä korkeita määriä piidioksidia ja alumiinia ja palavat lähes täydellisesti sintrauksen alkuvaiheessa toisin kuin yleisesti malmin pelletöinnissä sideaineena käytetty bentoniitti. Lisääntynyt tarve prosessoida huonolaatuista malmia on kasvattanut kiinnostusta orgaanisiin sideainesiin. Orgaanisilla sideaineilla valmistetut märät pelletit ovat tyypillisesti hyvälaatuisia mutta kuivina ja sintrattuina ne ovat kuitenkin liian heikkoja. Tämän diplomityön tavoitteena on selvittää kirjallisuuden ja laboratoriokokeiden avulla minkälaiset orgaaniset sideaineet tuottavat teollisuuden vaatimukset täyttäviä pellettejä.

Karbosimetyyliselluloosia (CMC) ja polymeerieja testattiin eri viskositeeteilla ja varaustiheyksillä, jotta näiden sideaineiden ominaisuuksien vaikutusta valmistettuihin pelletteihin voitiin arvioida. Pellettien laadun arvioimiseksi niistä mitattiin kokojakauma, kuinka hyvin ne kestävät pudotuksen, pölyävyys ja huokoisuus sekä märkien, kuivien ja sintrattujen pellettien puristuslujuudet.

Työssä tehtyjen testien perusteella 0.5 m-% liuoksen 30 cP viskositeetti olis sideaineelle optimaalinen, jotta se hallitsisi pellettien kasvua ja mahdollisimman suuri osuus pelleteistä olisi 10-12.7 mm suuruisia. Merkittävästi korkeammilla viskositeetteilla sideaine voi olla vaikea levittää tasaisesti, minkä lisäksi pellettien kuiva pinta rajoittaa niiden kasvua. Sideaineen viskositeetti ja varaustiheydes vaikuttavat eri tavalla pellettien ominaisuuksiin riippuen siitä onko kyseessä CMC vai polymeeri. Päinvastoin kuin kirjallisuuden perusteella, jonka mukaan negatiivinen varaus on sideaineen toivottu ominaisuus, kuivien pellettien lujuudet heikkenivät polymeerin varaustiheyden kasvaessa. CMC-sideaineille pellettien lujuuden riippuvuus varaustiheydestä on päinvastainen. Tämä ero eri tyyppisten sideaineiden välillä voi johtua niiden rakenteista: CMC:n rakenne on optimaalinen, sillä OH-ryhmät kasvattavat COO^--rymien affiniteettia rautaoksideja kohtaan. Testatuilla polymeereilla puolestaan on substituentteina elektroneja puoleensa vetäviä amidiryhmiä joista osa on korvattu COO^-ryhmällä. Näin ollen ryhmät heikentävät toistensa affiniteettia rautaa kohtaan.

Silaanit kasvattavat pellettien pinnan kosteutta hydrofobisuutensa vuoksi, jolloin haluttuja 10-12.7 mm pellettejä muodostuu enemmän. Aminosilaani kasvatti ainoataan pellettien pudotuskestävyyttä, kun taas ureidosilaani kuivien pellettien puristuslujuutta. Näin ollen kokeillut silaanit eivät ole järkeviä lisäaineita rauta malmin pelletöintiä varten.

Avainsanat Orgaaninen sideaine, pelletointi, rautamalmi, rautaoksidi

Foreword

The research for this thesis was carried out at Kemira reasarch and development center in Espoo from May to November 2016.

I would like to thank everybody at Kemira who gave me advice and help me executing the experimental part of the study. I would like to thank especially my patient thesis advisors M Sc. Jenni Lybeck and Matias Penttinen for their advice in both excecuting the experimental and literature sections of the thesis. I am also thankful for the past year with the great O&M team and to especially Veksi, Jouni and Tuula for teaching me all the different methods required in this study.

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Helsinki, 25.3.2016

Lotta Casey

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List of Abbreviations

CMC	Carboxymethyl cellulose
Fe_3O_4	Magnetite
Fe_2O_3	Hematite
FeO(OH)	Goethite
Na-CMC	Sodium carboxymehtyl cellulose
XRD	X-ray diffraction
XRF	X-ray fluorescence

1. Introduction

Iron ores generally contain vein minerals, such as silicates. For the steel industry the iron oxides must be concentrated, and in this process the ore is ground into fine particles *[1]*. The iron oxides are then reduced, at low temperatures by direct reduction *[2, 3]* or more commonly at high temperature in a blast furnace *[4]*.

In the blast furnace the concentrated iron oxides are chemically reduced and physically converted into liquid iron *[1]*. For a blast furnace the feed should have suitable particle size for the reducing gasses to flow through. The fine sized particles tend to pack tightly hence becoming nonpermeable and are also likely to be carried away by the high gas flow causing material wastage. To make the material suitable for the blast furnace it must be agglomerated back into larger particles *[5]*. Pelletizing and sintering are the two methods of agglomerating iron ore in general use for blast furnaces. Pelletizing is commonly used when the ore needs to be shipped great distances to the blast furnace due to the better durability of pellets *[5, 6]*.

The pelletization procedure consists of agglomerating the ore powder into “green” balls or pellets and drying and hardening them usually by heating. When wet, the ore particles are held together by capillary forces *[5]* and surface tension *[7]*, but they fall apart during the drying procedure. To help the particles stick together, small amount of binder is added to the moist iron powder before pelletization *[5]*. The powder is then granulated either in a rotating drum or a disc where the binder also controls their growth rates. The green balls are dried and then sintered, i.e. fired to temperatures as high as 1300 ˚C, fusing the particles together *[1]*. The resulting pellet should meet the requirements for blast furnace processing *[8]*.

The significance of pellet production has grown with the usage of low-grade iron ores as well as due to the increased consumption of iron and steel *[1]*. The iron pellet production alone was 440 MMt in 2012 *[9]*. The world’s crude steel production has nearly doubled in 12 years to 1,606 Mt in 2013 *[10]*[k]. These figures indicate a huge market potential for better binders.

Bentonite clay has traditionally been the most common binder for iron ore pelletizing. It however contaminates the product with silica and other undesirable elements, thus lowering the iron content *[5]* and adding additional material to the process. Addition of 1 % bentonite lowers the iron content of the pellet by 0.6 % *[11]* – which at the current production volumes

adds up to 2.6 MMt of additional material processed. Also lower iron content means a lower grade of iron that has to be sold at a lower price *[9]*.

Several organic binders that do not contain silica have been tested to provide an alternative to bentonite *[5]*. They often produce pellets with sufficient wet pellet quality, but generally they have sub-optimal dry and sintered strengths *[8]*. However, there are other benefits and the much lower amounts needed tend to compensate for the higher price of organic binders. Some anionic polymers and modified celluloses have given promising results and a few binders have been put to industrial production *[1, 5, 11, 12]*.

In this thesis the literature on organic binders is first reviewed to determine what kind of chemical structures and physical properties tend to be suitable for iron ore pelletization. Once the potential molecular structures are determined, they are tested as binders in the experimental section: The characteristics of the prepared dry pellets, such as dry strength, size distribution and the porosity are measured in order to determine the suitability of the binder and compare it to the existing commercial binders.

2. Iron ores

In order to understand the interaction between the organic binder and the iron ore it is important to understand properties of iron ore also. The iron in iron ores exists as different oxides such as hematite (Fe_2O_3), goethite ($FeO(OH)$), magnetite (Fe_3O_4) and maghemite *[13]*, with magnetite and hematite being the most important of the minerals mined for iron production *[14]*. The ores are complex combinations of different oxides and various gangue minerals *[15]*, such as silicates and calcium carbonate *[16]*.

In addition to the chemical structure other ore characteristics may vary significantly, such as moisture contents and acidity levels, particle specific surface area, size distribution *[5]* and shape *[6]*. The particle size and shape affect both wet and dry pellet strengths due to effects on packing density an interactions between particles. Wider particle size distribution generally enables denser packing, increasing the pellet strength. Particle shape and roughness effect friction forces between particles after drying. For example increasing the content of ultrafine particles from 45 to 65 ppm per gram in tactonite feed increased dry crush strengths of pellets from 2.27 to 6.80 kg *[6]*. Thus ores from different plants can be very different and a binder that works for one of them might not work for the other.

Magnetite and hematite behave differently in the pelletizing process due to magnetite oxidizing to hematite during pre-heating. This results in recrystallization which compensates for the burning of the binder and the lack of slag bonding. During recrystallisation strong bridges are formed between the concentrate grains and the crystals grow *[17]*. This phenomenon explains the improved pellet strength before the grains are sintered together even though there is little slag forming components. Forsmo *[18]* found that sintering started in the magnetite phase earlier (950°C) than in the hematite phase (1100°C). Thus inducing slag bonding would be particularly important to increase the compressive strength of pellets when pelletizing hematite ores. This can be done by introducing inorganic additives to the pellet *[8]*.

During fragmentation of magnetite and hematite some of the Fe-O bonds are broken down and are hydrated to form amphoteric hydroxyls (FeOH) in aqueous systems. These hydroxyls can then act as an acid or a base depending on the conditions *[19]*. At low pH these surface sites are protonated taking the form $Fe\text{-}OH_2^+$ and at high pH they are deprotonated forming $Fe\text{-}O^-$ sites. The dissociation reactions are shown below.

$$FeOH + H^+ \leftrightarrow FeOH_2{}^+ \quad (1)$$

$$FeOH \leftrightarrow FeO^- + H^+ \quad (2)$$

In consequence of these amphoteric surface sites, the oxide particles become either positively (1) or negatively (2) charged depending on the reaction that takes place. Charged inorganic and organic ions can be adsorbed to these sites *[13]*] forming an electrical double layer (EDL) at the metal/polymer interface. The surface electrical properties of oxides can be studied by measuring their zeta potential. In this procedure the electric double layer is studied instead of the actual oxide surface by measuring its potential difference *[20]*.

The pH at which the net surface charge of the oxide reaches zero in the absence of these adsorbing ions, is called the point of zero charge (PZC) *[13]*]. Another term explaining pH dependence of surface charge is the Isoelectric point (IEP). Parks stated the PZC and IEP for solids to be identical by definition *[21]*, whereas according to Babic they are equal only in the absence of specific adsorption of counter ions *[22]*.

For magnetite values of PZC between 4.4 and 8 have been reported *[13, 23]*. This may be due to differences in the iron ore composition and structure. At this pH positive and negative sites are found in equal numbers. At pHs lower than the PZC, the pure oxide surface is charged positively (1) and negatively (2) at pH above it *[13]*]. Thus the pH of the concentrate effects what type of ions are adsorbed on the surface sites and consequently the structure of an optimal binder. The adsorption of the different ions is also pH dependent due to the effect of electrostatic interaction. Examples of zeta potential curves for magnetite and hematite and the effect of adsorbed amines are shown in the following figure.

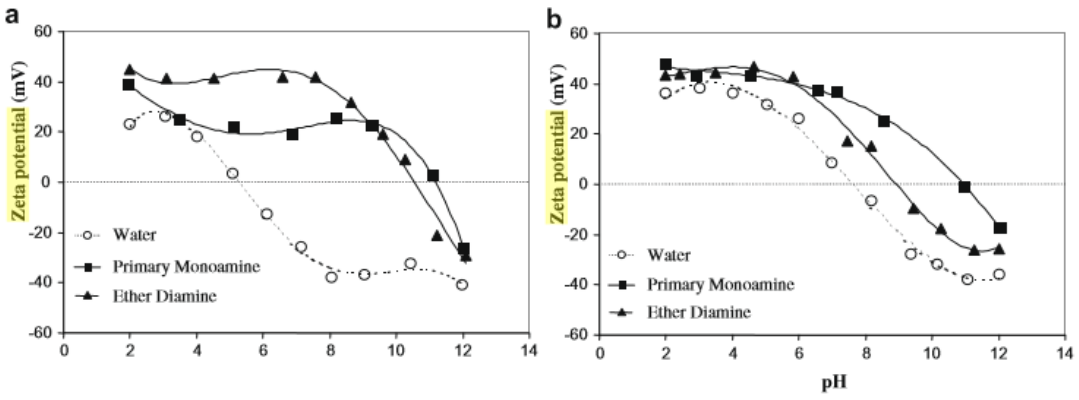


Figure 1. Zeta-potential of magnetite (a) and hematite (b) as a function of pH in the absence (dotted line) and presence (solid line) of 10 4 mol/L amine acetate *[19]*.

The surface charge has a major effect on the interaction of an particle with other charged particles and their adsorption onto the iron ore. Tombácz *et al.* have reported organic anions to be adsorbed on the iron ore through complex formation *[24]*, whereas according to Illés *et al.* Coloumbic attraction between oppositely charged surface and organic ligand may contribute to the interaction depending on the conditions *[13]*]. The adsorption changes the oxide surface charge state thus affecting further interaction. When polyanions are adsorbed on the ore surface, the coated concentrate particles become negatively charged due to excess acidic groups, which cannot bind to the surface due to steric reasons *[24]*.

In addition to the surface charge the zeta potential indicates what type of interaction the particles have with each other. Suspensions with zeta potential above 30 mV or below −30 mV are considered stable due to the repulsive forces between particles while dispersed *[25]*. Thus the zeta potential of a concentrate should be between -30 and 30 mV when pelletized.

3. The requirements for iron ore pellets

The pellets should have good compressive strength when wet, dry and sintered in order not to deform under the static pressure or disintegrate when dry. Pellets that grow fast tend to also have low compressive strengths when sintered, which causes them to get crushed easier during handling, adding to the amount of fines produced *[11]*. They should not be so plastic that they deform under pressure caused by the pellets on top, but should have enough elasticity so that they do not spall under impact during balling or other handling. The disintegrating and spalling would cause generation of dust and fines which then decrease bed permeability required by the blast furnace and coat the furnace walls increasing wear and thermal loads. The pellets should have dry smooth surface, for the abrasion and dust pick up to be low. For optimal blast furnace processing the pellets should also have small size distribution and be porous and round *[5]*.

The green balls are subjected to considerable loadings from the handling during agglomeration, sizing and conveying between balling and drying units. In addition to this stress the balls on the bottom of the traveling grate experience static loadings. The pellets are subjected under loadings also after firing as they are usually shipped considerable distances from the pelletization site to the blast furnaces *[1]*.

Good reducibility is another desirable property of pellets as it means less processing time is required in the blast furnace. Reducibility rate indicates how easy the oxygen removal from the iron oxides is. Porosity has been found to affect the reduction rates due to the area in contact with the gasses *[1]*.

The pellets should have a narrow size distribution with most of the pellets with 9-12 mm diameter. Generally 90 % of industrial pellets are within this size range. The wet, dry and sintered strengths can be measured with a compression test and the plasticity of the green balls can be measured with a drop test and resistance towards abrasion with tumble index. Commonly accepted threshold values for large-scale iron ore pelletization are 1 kg/pellet for wet *[18]* and 250 kg/pellet for fired compressive strengths. For the minimum dry pellet strengths different limits have been announced but they tend to be between 2 *[6, 8]* [j, o] and 3 kg/pellet *[18]*. The tumble index is given by the percentage by mass of the over 6.30 mm fraction after tumbling the pellets in a drum *[26]* and the values should exceed 95 %. This means less than 5 % of pellet weight should be turned into dust during a tumbling index test *[1]*.

The drop number (average number of drops from a given height before breakage) describes the plastic and elastic behavior of green iron ore pellets. The pellets need to have some elastic behavior for them to withstand the loading from one conveyor belt to another. It is required also so that the pellets would not spall when bouncing around in the balling drum during pelletization. For the pellets to last this handling the drop number needs to be higher than 5 *[18]*. While the drop number needs to be high enough to resist the rough handling, it should not be so high that the pellets become prone to irreversible plastic deformation. This starts to occur for pellets with high drop numbers, with the limit set in the industry as 10 *[27]*. The plastic deformation occurs due to the load caused by the above-lying green pellets in a static bed of pellets. Pellets that are too plastic become oval under the load which leads to decreased permeability of the bed *[18]*. Thus the drop number should be something between 5 and 10.

Often when some of the pellet qualities are improved by changing the binder, its dosage or moisture content of the pellets, some of the other qualities are decreased simultaneously. For example compressive strengths are often lower for pellets with higher drop numbers. A few examples are gathered in the table below.

Table 1. Drop numbers, wet, dry and sintered strengths of pellets produces with CMC binders at different dosages and moisture contents *[12]*.

Binder	Explanation	Dosage (%)	Moisture (%)	Drop number	Wet strength (kg/pellet)	Dry strength (kg/pellet)	Sintered strength (kg/pellet)
CMCC1	CMC with most sodium carbonate	0.10	7.7	3.4	1.0	1.5	207.3
CMCC1		0.30	8.7	6.1	1.2	4.7	181.9
CMCH	The most pure of the CMC binders	0.10	7.0	3.3	1.3	2.4	317.5
CMCH		0.10	9.0	7.0	1.9	3.2	305.3
CMCH		0.15	8.1	4.1	1.0	5.7	267.6

Increasing the dosage of CMCC1 causes an increase in the pellet moisture, which increases the drop number of pellets. However, the compressive strength of sintered pellets is slightly decreased most likely due to higher porosity. Same is observed when CMCH dosage is increased from 0.10 with a more significant difference and the wet strength decreased slightly as well. Also keeping the dosage of the CMCH constant while increasing the moisture content of pellets results in higher drop numbers but lower slightly lower sintered strength. Thus rather than trying to produce pellets with as high compressive strengths as possible, the pellet qualities should be optimized so that all of them meet the requirements.

4. Bentonite and organic binders

Practically anything that causes particles to adhere into a mass can be classified as a binder. The binders can be classified by the binding mechanism into inactive and chemical film binders, inactive and chemical matrix binders and chemical reaction binders. The main differences are in required binder dosage, the compaction pressure required and whether a reaction takes place, typically making the binding irreversible. Thus not all binders can be used in all applications *[5]*.

Inactive film binders, such as bentonite, are used in iron ore pelletization. These binders form a sticky layer on the particles, binding them together with different forces (capillary, adhesional or cohesional). The inactive film binders are typically effective even with low dosages, bind particles together rapidly as no chemical reactions need to take place and do not generally require high compaction pressures *[5]*.

Bentonite is a aluminosilicate clay, consisting mainly of montmorillonite, $(Na,Ca)_{0.33}(Al_{1.67},Mg_{0.33})Si_4O_{10}(OH)_2 \cdot nH2O$ *[28]*. It absorbs a lot of moisture present in the iron concentrate simultaneously improving the physical properties of the pellets *[11]*. Bentonite melts during the heating process enveloping the particles inducing slag film bonding *[8]*.

However, it contains approximately 60 % silica *[29]* and at a common dosage of 0.5 to 1.5 w-% *[17]*, it increases the silica content of produced pellets by approximately 0.5 %. This is rather counterproductive as the purpose of iron ore processing is to remove silicate minerals form the ore. For the blast furnace to operate efficiently, the iron concentration of the feed needs to be above 58 %. This may sound very low but as the iron is in an oxide form, for example hematite is only approximately 70 % iron hence the acceptable gangue content is quite low. Adding bentonite to the agglomeration feed is especially detrimental for iron ore concentrates with high acidic content, as their silica and alumina contents are already high *[1]*.

Replacing bentonite with a silica-free binder allows the silica content of the agglomeration feed to be raised. This possibility would lower the need of grinding used to liberate silica, again increasing production capacity and lowering costs *[5]*. Silica-free binders are becoming more interesting due to iron ore source depletion *[30]* and increasing volumes of processed low grade iron ores.

Organic binders do not generally contain silica and 85-100 % of their mass is combusted during the high-temperature firing process *[11]*. Pellets bound with organic binders generally have the required qualities when wet, but have insufficient compressive strengths when pre-heated (heated up to 1000 °C) and sintered *[11, 31]*. This may be due to increased porosity and low disintegration temperatures of organic binders. Higher porosity means less contact between ore particles *[32]* and the greater distance may also retard the sintering reactions *[12]*. Organic binders tend to burn at around 300˚C, leaving the pellet virtually unbound and fragile until magnetite starts oxidizing and strengthening the pellet through recrystallization in about 375 ˚C *[5]*. Another factor explaining the weakness of pellets bound with organic binder is the lack of slag film bonding due to low content of ash and other impurities *[8]*, which form a liquid slag phase which helps bind the ore particles by wetting them *[33]*. However, while slag improves pellet strength it retards their oxidation rate *[18]*.

While organic binder pellets need to be fired in higher temperatures to achieve required strengths, lower silica content means less valueless material is heated in the furnace and the filling degree is increased. Both this and the higher reducibility increase production potential and reduce processing costs. Hence the iron makers at the Middletown Blast Furnace have been able to increase the hot metal production by 2.6 % and the fuels costs have been reduced 6 % using pellets made with organic binders. Though the organic binders are

generally more expensive than the relatively cheap bentonite, lower dosages are required to achieve the optimal binding *[1]*.

With several carboxymethyl cellulose (CMC) binders requirements were met with just 0.1 w-% and even lower dosages *[12]*. The low dosages of organic binders compensate for their higher price. However, getting such small amount of binder evenly distributed throughout the iron ore concentrate may be difficult. While some researchers have argued that uniform dispersion of the binder is necessary, two studies have proven that the required standards can be met with uneven distribution of binder. High intensity mixing further lowers the required binder dosage *[1]*.

There are several benefits with using organic binders but they have also some problems that need to be solved before they can replace bentonite completely for all pellet grades reduced in a blast furnace. Currently organic binders are competitive when the silica content of the concentrate is high, so that it is cheaper to use organic binder than remove enough silica to meet the requirements with added bentonite.

Several organic binders that have not filled the requirements for blast furnace may be more suitable for direct reduction. These process do not require as high compression strength as the blast furnace. Also dust causes fewer problems than in blast furnaces and the pellets can be hardened by cold-bonding. As the pellets are not melted during reducing, the slag cannot be separated and required purity of pellets is higher than for the blast furnace, hence bentonite is not suitable for the process.

5. Requirements for the organic binder

There are several requirements an organic binder should fill for it to produce pellets with required quality. These requirements include chemical, physical and economical aspects.

Binders function is to hold the particles together and control the growth of the pellets. It should not cause contamination or sintering problems and the processing of the product should not be too complicated *[5]*. The binder should also increase wettability of iron ore particles *[34]* and pellet porosity important for good reducibility *[5]*, and possess good thermal stability and absorption capacity *[34]* but still release the moisture during heating *[5]*.

The binders have several properties that affect the pelletisation and thus the pellet properties mentioned previously. These include viscosity, water adsorption, the forces between the binder and the iron ore as well as the binder molecules, the melting temperature or glass transition temperature and molecular weight. In addition to these properties the binder's molecular structure has a major effect on its interaction with the ore. The functioning of the binder can be enhanced or compensated using additives. These properties are discussed in more detail in the following chapters.

5.1 Viscosity and moisture

Viscosity is a characteristic of a fluid used to describe its resistance to change shape or movement of neighbouring molecules relative to each other *[35]*w]. The viscosity of the binder solution affects the movement of moisture within pellets, which has an impact on the ballability of the concentrate, controlling the pellet growth and the pellet quality. Ballability is defined as the ability of particulate matter to form pellets. The main parameters affecting the ballability of iron ore are its fineness, moisture content, binder dosage and good wetting of the particles. The optimum moisture content for each raw material depends on the particle size and size distribution, inner porosity of particles, their surface roughness and wettability. The finer the material the higher the moisture content required to achieve good ballability, because of the higher surface area in need of wetting *[18]*. Excess surface moisture however induces rapid green ball growth which results in weak pellets with rough surface, which then produces more fines – hence it is important to control the pellet moisture content and its transportation to the surface *[1]*.

Binders that increase the viscosity of the moisture within the pellets slow down its transportation from the green ball interior to the surface. Thus binder solutions with high viscosity tend to produce pellets that grow slowly (low balling rate) with high recycling loads. This tends to make the green balls strong and spherical with smooth surfaces. Slow ball growth is vital also to produce pellets with small size distribution *[11]*. This is important because a bed with uniform pellets is more permeable and hence the pressure drops and energy consumption in the blast furnace are smaller and airflow more uniform *[5]*. Binder viscosity and pellet drop number seem to be indirectly related *[12]*, with high viscosity binders producing pellets with high drop numbers (figure 2) *[36]*.

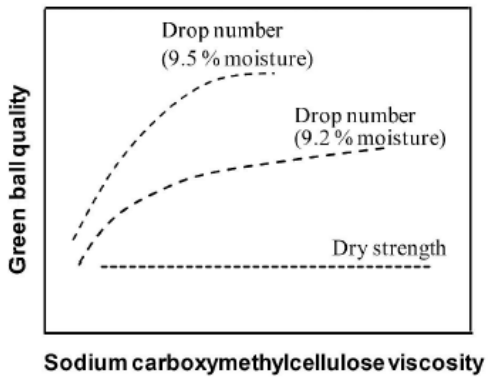


Figure 2. Effect of CMC viscosity on green ball drop number and dry strength *[36]*.

The dry strength does not seem to be affected by the change in viscosity whereas the drop number increases first significantly with viscosity and slows down at higher viscosities. The initial increase is steeper with higher moisture content but levels off earlier. Goezman *et al. [36]* suggested the higher moisture level enables the binder to extend into the liquid more fully attaining higher thickening effect *[1]*.

For the binder to be effective it must get into intimate contact with the iron ore particles. This means the binder solution needs to have good wettability towards iron ore. A liquid tends to adopt a drop-like shape when coming into contact with a solid. The tangent of the drop surface is called contact angle θ (figure 3) *[11]*.

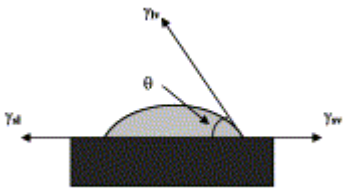


Figure 3. The contact angle of a liquid on a solid surface *[11]*.

Liquids with low contact angles spread readily across the surface wetting it, whereas high contact angles imply the liquid will tend to form beads instead of wetting the surface. Thus binder should reduce its solutions contact angle on the iron ore surface as much as possible for it to have good wettability. To achieve this the binder should make the ore more hydrophilic when absorbed at the surface sites of the oxide. Thus hydrophilic functional groups such as OH need to be introduced into the molecular structure *[11]*. Increasing the hydrophilicity of the concentrate surface is important also in order to achieve efficient balling and high strength of wet and dry pellets. If hydrophobic areas are present within the

concentrate, air bubbles may become attached to them and be incorporated inside the green pellets during wet agglomeration. The inclusion of air would than lower the pellet strengths significantly *[37]*.

The contact angle depends both on the binder solution and the iron ore surface. The density of surface hydroxyl groups and relative number of oxide bridges between the metal atoms on the ore surface effect its wettability. Iveson *et al.* measured the wettability of three different iron ore powders by comparing the air pressures required to stop the capillary flow of water and cyclohexane through beds of packed powder. The calculated contact angles of the ores ranged from 30 to 70°, correlating with the relative amounts of haematite and goethite: the higher the goethite content, the smaller the contact angle. This due to the mineral structures: haematite (Fe_2O_3), and iron oxide, has two hydroxide groups bonded to each atom, whereas goethite (FeO(OH)), an oxy-hydroxide, probably has a higher density of hydroxide species *[15]*.

Thus in order for a solution to be wettable it needs to spread on the solid surface, losing its droplike shape. For this to happen the solution work of cohesion must be less than the work of adhesion between the liquid and the solid *[11]*. Thus even though high viscosity is generally a selection criteria for a binder, it increases its work of cohesion which in turn increases the required work of adhesion to achieve good wettability. Solutions with high viscosity also enter capillaries slower *[18]*. High viscosity can also cause problems in cases where the binder is added as a solution as it would be difficult to spray evenly on to the iron concentrate. However this should not be a significant problem as the binder is generally added as a dry powder and the moisture is adjusted afterwards *[5, 11, 12]*.

5.2 Absorption of water

Water absorbability of the binder is an important property in controlling the free moisture present in the agglomeration feed. It can be described using the plate water absorption test (PWAT), which is calculated from the percentage of weight gain when nearly immersed in water and allowed to adsorb water for a specific time up to 24 hours *[12]*.

As stated previously, it is important to control the growth rate of agglomeration as high rates tend to produce weak pellets with rough abrasive surface. In order to control the balling it is important to control the free moisture present in the agglomeration feed as too high surface

moisture content induces rapid green ball growth. In addition to high viscosity of the binder, its high absorption of water can slow down the transportation of moisture thus help keep the balling rate low. With less absorbent binders more excess moisture is exuded to surface of pellets, where it then causes the green balls to enlarge rapidly and enables them to coalescence in extreme cases even turning the agglomerating material into “mud”. Too little moisture causes problems as well, as the nucleated seeds are difficult to enlarge without sufficient wetting of particles and the produced pellets become porous and weak *[1]*. Thus the optimal moisture for agglomeration depends on the binder.

In addition to high viscosity high PWAT value and swelling of the binder seem to give high drop numbers. However, the pellets with high drop numbers often have low dry and fired strengths. Haas et al. suspected that this is because binders with extremely high absorption (such as starch acrylic copolymers) expand a lot during pelletization causing the iron oxide particles to move apart. The expanded binder then shrinks extensively during drying, which makes the pellet porous and may tear the binder away from the iron particle surfaces *[5]*. The greater distance between oxide particles may retard the sintering reactions which would explain their low dry compressive strengths *[12]*. Another nonexclusive explanation is poor particle-particle contact resulting from high pellet porosity *[32]*.

The most common failure of pellets during heating is spalling where the outer layers of the pellet flake off due to fluid evaporation. It occurs when steam is released faster than it can escape the green ball structure causing pressure build up *[1]*. The pressure drop resulting from a fluid flowing through a porous system of equal-sized spheres can be estimated using the following Kozeny-Karman equation for thermal spalling

$$\Delta p = K \frac{\eta}{d^2} \frac{(1-\varepsilon)^2}{\varepsilon} Lv \qquad (1)$$

where K is the Kozeny-Karman constant, η viscosity of the liquid phase and v the velocity of its flow, d the particle diameter, ε porosity of the pellet and L its depth *[5]*. From this equation it apparent that large concentrate particle size, high viscosity of binders and high porosity of pellets can increase the probability of thermal spalling. As high absorption of the binder makes the pellet more porous, it also induces spalling.

5.3 Adhesive and cohesive forces

There are cohesive forces within the binder and iron ore layers and adhesive forces at their interface. Adhesive force refers to the binding force at the interface between the ore particles and the binder. It is the sum of van der Waals, electrostatic, magnetic and viscous forces as well as hydrogen and chemical bonding between the binder and the ore particles *[11]*. The binder cohesive force is the net interaction force between the binder molecules and is a measure of the mechanical strength of the binder itself *[38]*. The failing of the binding system and resulting breakage of the pellet can result from an exterior force exceeding either of these two forces needed to keep the pellet intact (figure 4). The cohesive and adhesive failure may also occur at the same time if either the strain is spread unevenly inside the binding system or the forces are equal in magnitude *[39]*.

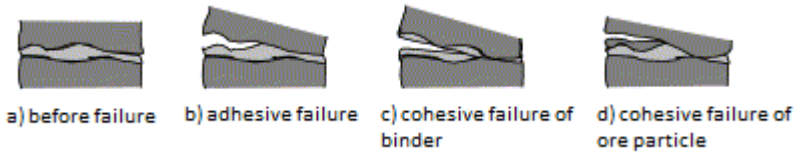


Figure 4. Type of failures for a binding system *[39]*.

There are also several other forces present in the binding system but they tend to be either negligible or so great that generally do not account for the observed failure. These forces include ore cohesive force within the ore particles and interaction force between ore particles. The interaction force is sum of mostly negligible forces between ore particles such as van der Waals, electrostatic, magnetic and mechanical interlocking forces, but also capillary forces. The capillary forces have been shown to be significant in wet pellets whereas in dry pellets they are no longer present making the interaction force of dry pellets negligible compared to the cohesive and adhesive forces. The ore cohesive force is equivalent to the binder cohesive force but within the ore particle. The cohesive strength between the iron ions is inherently great, hence the failure takes place either inside the binder layer or at the interface *[11]*.

Thus to produce strong pellets it is important for the binder to have chemical bonding both to the ore particles and other binder molecules. In order to achieve this polar and hydrogen bond forming functional groups should be introduced to the binder structure. In addition to its chemical structure, the mechanical strength of an organic polymer depends also on the

molecular weight, crystallinity and extent of crosslinking or branching of the binder *[11]* and viscosity of its solutions. High viscosity solutions tend to have great cohesive force between the molecules *[18]*.

For the binder to have good adhesion properties needed to produce strong pellets, it also needs to be wettable towards the ore, behaving like a surfactant *[11]*. This means it needs to spread over the particles getting into contact with as large surface area of the particles as possible. Hence though good cohesion of the binder is important for the pellet quality, its work must be less than the work of adhesion of the liquid on the solid. In order for the binder to behave like a surfactant in addition to reducing the contact angle, it should also lower both the solid/liquid and liquid/air interfacial tensions by being absorbed at the interfaces *[11]*.

However as bentonite dosages are increased above 0.5 %, the viscosity and cohesive force of the binder liquid keep increasing, but the adhesion of the binder on the iron ore may become weaker resulting in adhesive failure *[18]*. This can be explained by incomplete wetting of the ore. In the case of ore particles the binder liquid needs to penetrate between the particles to get into contact with them *[11]*. The rate of entry of a liquid into a capillary can be estimated with the following equation

$$\frac{dl}{dt} = \frac{r\gamma_{lv}cos\theta}{4l\eta} \qquad (2)$$

where γ_{lv} is the interfacial tension at the liquid/vapor interface, θ the contact angle of the droplet, η the viscosity of the solution, r the capillary radius and l the length filled by liquid *[40]*.

From the equation it is quite evident that though in order to behave like a surfactant the binder should lower the interfacial tension of the liquid/vapor interface, it needs to be high for the binder solution to be able to penetrate between particles. Thus in addition to reducing the contact angle, the full wetting of the particles is favoured by low viscosity of the binder solution, and increasing the surface tension of the liquid, while still keeping the solid/liquid interfacial tension low.

5.4 Chemical structure

The optimal binder chemical structure can be logically derived from the requirements set for the binder. Qui et al. have suggested a general structure for an ideal organic binder (figure 5). Polar and hydrophilic groups should be bound to the organic backbone. The backbone should be strong and heat resistant so that the binder will not become fragile during thermal treatment of the pellets. The polar group should be able to bind chemically to the iron particles whereas the purpose of the hydrophilic group is to increase the wettability of the binder *[11]*.

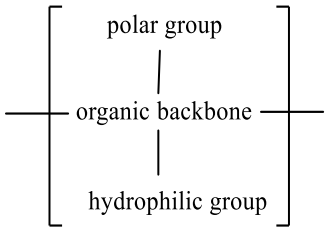


Figure 5. Ideal organic binder structure.

It is generally believed that the organic backbone should be thermally stable so that it does not disintegrate during drying and according to Quit et al. also mechanically strong. This might not be as important as led to believe in most articles *[1, 11, 41]* as the decrease in pellet strength can be compensated by adding slag forming constituents *[42]*. However, the ideal situation would be for the organic binder to last temperatures that the sintering starts to take place in. Thus as the binder starts to burn weakening the pellet the sintering would reinforce it and no non-combustible additives that increase impurities would be needed.

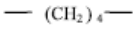
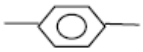
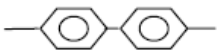
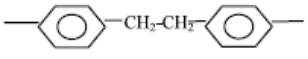
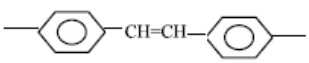
Double and triple covalent bonds are much stronger then singular bonds (table 2). The bond energy is defined as the heat required breaking one mole of molecules into their individual atoms *[11]*.

Table 2. Bond lengths and energies of different bond types *[11]*.

Carbon bond	Bond length (Å)	Bond energy (kJ mol^{-1})
C–C	1.5	348
C=C	1.3	606
C≡C	1.2	828
C–H	1.1	412
C–O	1.4	333
C=O	1.2	705
C–N	1.4	292
C–F	1.4	441
C–Cl	1.8	328
C–Br	1.9	275
C–I	2.1	240

The triple bond can stand almost double the energy (heat and stress) before breaking compared to the single bond. The non-single bonds and ring structures also prevent the rotation of bonds making the structure rigid and hence able to resist stress force better. The effect of reducing single bonds by replacing them with aromatic rings and double bonds can be seen from the table where crystalline melting temperatures (T_m) for polyesters with the aliphatic chain replaced with different aromatic ring structures are shown (table 3). Replacing the aliphatic chain (A) with an aromatic ring (B) increases the thermal stability greatly raising the T_m with 220 ˚C. Adding an aromatic ring so that they are coupled (C) further increases the T_m by 85 ˚C. Making the aromatic structure more flexible with an aliphatic unit between the two rings (D) lowers the T_m by approximately 115 ˚C. If the aromatic rings are connected with an unsaturated double bond instead of an aliphatic unit (E) the T_m is nearly doubled *[11]*.

Table 3. Effects of backbone structure on T_m of polyesters derived from ethylene glycol *[11]*.

Compound	Main-Chain Unit	T_m (°C)
A		50
B		270
C		335
D		220
E		420

Making the backbone structure branched, networked or gel-like may prevent the binder being adsorbed completely to the ore particles; reduce hydrophobic bonding between binder molecules and make the binder retain the green-ball water better *[1]*.

The iron ore minerals, hematite and magnetite are quite polar and thus naturally hydrophilic and exhibit strong covalent or ionic surface bonding *[43]*. In addition to good wettability, good adhesion requires that binder molecules have polar groups that form chemical bonds with the iron particles. Polar groups that react with iron ions include for example $-COO^-$, -OH, $-CONH_2$, $-NH_2$, $-NO_2$, =NH, $-N^+R_3$, $-PO_3H$, $-SO_3H$, $-OSO_3H$ and -SH. Sulfur and phosphor have a harmful impact on iron and steel quality. Thus the last four functional groups are not suitable as functional groups of binders. According to ionization potential and electron affinity calculations made by Qui *et al.,* COO^- should easily react with iron ores. The researchers also calculated the bond iconicity of the interaction and evaluated it would be ionic *[11]*.

According to Nazarov the adhesive interaction between the binder and ore in the presence of water is determined by the isoelectric point (pH_{IEPS}) of a hydroxylated oxidized metal surface and the acid dissociation constant (pK_α) of the polymer's polar group. The maximal adhesion of functional polymers is achieved at maximum pH_{IEPS}-pK_a difference *[20]*. This means the stronger the acid (lower pK_a), the better it adheres to oxides with low pH_{IEPS}. This would support the calculations of Qui et al. as carboxyl acids generally have high pK_a.

The adsorption mechanism can consist of complexation *[24]*, hydrogen bonding *[44]* and coulombic attraction *[13]*] between the functional groups and the surface sites of iron oxide. The significance of the different mechanisms may depend on the functional group in question as well as the conditions such as pH, which affects the general charge of the oxide surface. In addition to these forces the adsorption of water-soluble polymers on hydrophilic surfaces, such as iron ore, depends also on solvation forces, which reduces adsorption *[44]*.

Polyacrylamides are nonionic and bind to the surface sites through hydrogen bonding. Though it is not considered to be an electrostatic interaction, the carbonyl group is partially negatively charged and thus its interaction with the oxide hydrogen groups depends on the relative positivity of the surface sites. Thus adsorption of such nonionic polymers is pH dependent and characteristic to the iron ore *[44]*.

Most polar groups are also hydrophilic. The type of the hydrophilic group and their relative position affect the functioning of the binder. Electron-withdrawing hydrophilic groups, such as NO_2 and $COOH^-$ reduce the polar group affinity towards iron ore whereas electron-donating groups such as NH_2 and OH have an increasing effect. Thus having only COO^- would mean the groups have an affinity decreasing effect on each other when they are close to each

other. Therefore an electron-donating group such as either NH_2 or OH should be bound to the organic polymer chain in addition to COO^- *[11]*. The electron-donating group should be quite close to the hydroxylic group for it to have an effect on the binding to iron. Two of the possible structures for ideal organic binders, with these functional groups drawn in are shown below. The hydroxide and amine groups could be changed around to get two new structures.

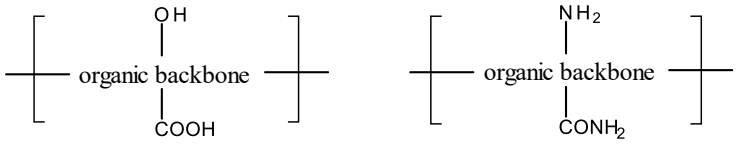


Figure 6. Ideal organic binders with functional groups shown.

The function of the binder is affected also by the relative position and amount of the hydrophilic and polar groups. When they are far apart the interaction between the two functional groups is weak. However, if the different functional groups are located at each end of a long molecule it may bend around the iron ore particle surface with the functional groups orientated towards the ore surface. In a situation like this the non-polar carbon chain makes the iron ore surface hydrophobic *[1]*, which would cause problems as the agglomeration feed needs to be hydrophilic.

In addition to increasing the polar group affinity, having multiple functionalities in the structure can also help uncoil organic binders dissolving and dispersing them more rapidly into the agglomeration feed *[1]*. This is important in the industrial scale as often there is not much time provided for binder uncoiling which is important to distribute the binder evenly into the pellets.

The number of different functional groups affects the solubility and adsorption of the binder as well as its sensitivity to salts. Producing binders is in some cases done by modifying an existing structure such as cellulose. Degree of substitution (DS) is used to describe the extent of the modification. It describes the average number of substituents per monomeric unit, or in the case of condensation polymers, per base unit. The term is mainly used in cellulose chemistry *[45, 46]*. Sodium carboxymethyl cellulose (Na-CMC) for example is produced from cellulose by replacing some of the hydroxyl groups (-OH) with sodium carboxymethyl groups ($-CH_2COONa$) *[1]*. Thus the higher the DS, the more anionic and water soluble the cellulose is. As each cellulose unit has three hydroxyl groups its theoretical maximum is 3.0.

As the binders adsorbed on the oxide surface change its surface charge state, they also affect the aggregation of the mineral particles *[7]*. During pelletization the ore particles are brought together, thus promoting the aggregation of ore particles would be expected to increase ballability of the concentrate. The colloidal properties of iron ore affect its aggregation. As colloids are stabilized by high surface charge *[13]*], the binder ideally would decrease repulsion between particles by rendering them neutral, which should increase the aggregation and thus ballability.

5.5 Thermal stability

The binder should hold the agglomerated particles together during drying until the pellets are heated to high temperatures to sinter the grains together. This means optimally the binder would not disintegrate in low temperatures during drying (105 ˚C) but on the other hand it should be eliminated during sintering (up to 1300 ˚C) *[5]*.

Solutions with linear polymers have good viscoelasticity at room temperature and consequently mechanical properties of green pellets are good. However, when heated, polymers soften, melt, oxidise chemically, degrade and decompose. This weakens the mechanical strength of the binder, causing it to lose its viscoelasticity. Losing its viscoelasticity makes the binder fragile thus reducing the mechanical strength of pellets. Thus the binder optimally would have high melting point or glass transition temperature as well as be stable thermally and towards oxidation *[11]*. However as this tends to be difficult to achieve with organic compounds while keeping the price reasonable, additives can be added to increase the binder strength during drying and sintering *[1, 37]*. The minimum thermal stability for the organic binder is to last until the moisture has evaporated at 105 ˚C *[5]*.

To achieve high reducibility the pellets must not collapse too early, as it would reduce the permeability of the bed and thus the reducibility of the pellets *[1]*. Hence high softening temperatures are preferred to prevent early collapsing of the pellets *[12]*.

5.6 Molecular weight

The molecular weight of the polymer affects its viscosity and solubility as well as other mechanical and thermal properties. Viscosity, mechanical and thermal properties tend to increase with molecular weight whereas solubility decreases *[1]*. As stated previously high

viscosity binders tend to produce pellets with high drop numbers. Thus drop number of pellets can be increased with using larger binder molecules *[12]*. The green ball drop number depends on the molecular weight and dosage of the binder (figure 7). The drop number increases more with dosage for high molecular weight binders *[36]*.

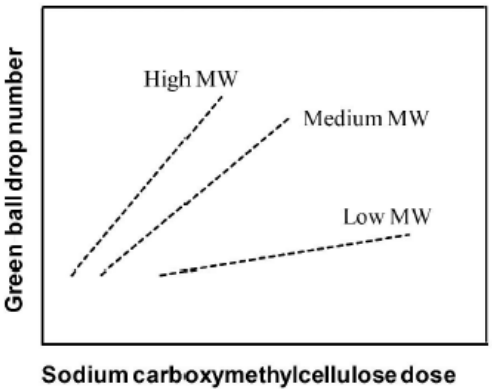


Figure 7. Effects of Na-CMC viscosity and molecular weight on drop number of green balls *[36]*.

The other mechanical and thermal properties the molecular weight of the binder may affect are cohesive force, mechanical strength and thermal stability. To achieve high tensile and shear strengths the adjacent chains must have interaction between them. These interactions are greatly increased with molecular weight and branching as the longer and more branched chains tend to get tangled with their neighbors helping dissipate the stress forces (figure 8). The chain entanglement may also increase adhesion at the interface. Mechanical strength of organic polymer depends also on its crystallinity *[11]*.

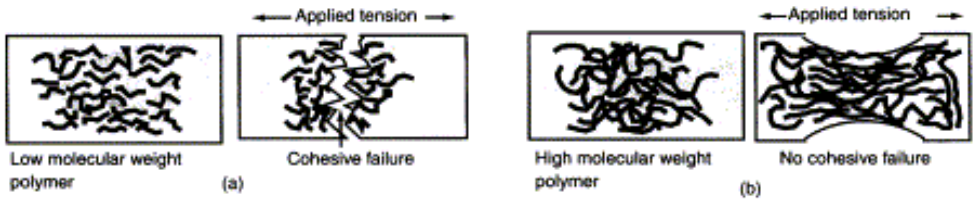


Figure 8. Effect of molecular weight on polymers cohesive strength *[11]*.

Increasing the size of the polymer and making it branched enhance their thermal stability and mechanical properties. Nevertheless, the viscosity and solubility tend to set a limit on the polymer size suitable for a binder. To prepare the pellets and achieve good wettability the binder must be water soluble and not too viscose so that the solution is able to surround

the particles for it to be wettable. Thus the suitable molecular weight depends also on the polar and hydrophilic group natures and the structure of the skeleton chain.

6. Examples of organic binders

Wide investigations have been done to develop or discover binders not containing silica. Some of them are available from natural resources, some formed as waste material in other processes and some manufactured for the specific purpose. In principle the naturally occurring materials are expected to be producible at a lower cost than synthetic polymers as they do not require as much processing. However, in some cases limited sources, competition with other markets for the same material and shipping costs increase prices. A large range of materials from synthetic polymers to cattle manure have been tested as binders for iron ore pelletization and a few of them have been put forward to commercial production *[5]*.

6.1 Celluloses

Cellulose, a natural polymer, is readily available in most parts of the world. It is digested with sodium hydroxide and the formed smaller polysaccharides are made water soluble by introducing new functional groups via ether group formation. Reaction between cellulose and mono-chloroacetic acid produces sodium carboxymethyl cellulose (Na-CMC). The structure of the formed carboxymethyl cellulose binder is shown in figure 9 (B). Both cellulose and Na-CMC can be modified further in order to control the properties of the polymer and its solutions and enhancing its functioning as a binder for iron ore pellet production *[1]*.

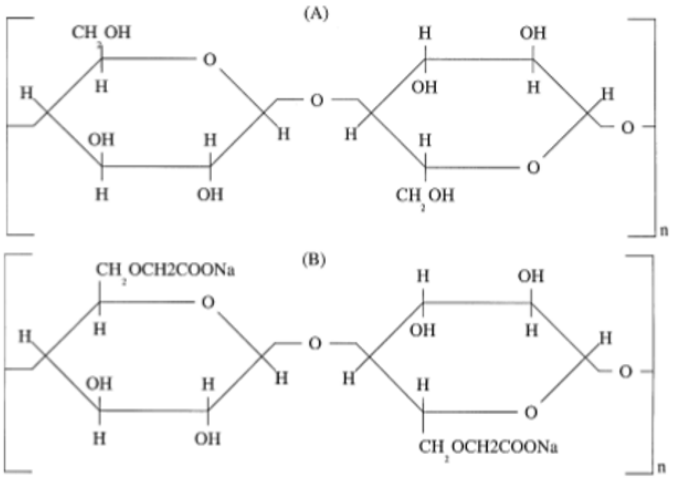


Figure 9. Idealized chemical structures of base units for (A) cellulose, (B) sodium carboxymethyl cellulose (Na-CMC) *[12]*.

The unmodified cellulose has only hydroxyl substituents that could bind to the iron and it is not soluble in water. Modifying the cellulose by changing a proportion of the hydroxyl groups into carboxylate anions through an ether formation reaction makes the polymer soluble in water and incorporates the optimal COO^- group for binding to iron ore into the structure. Increasing the degree of substitution increases its solubility and decreases unwanted interactions with different ions in the solution. Generally cellulose needs to have DS above 0.4-0.5 in order for it to be soluble, unless great effort is made to achieve even substitution along the backbone. Though CMC has the required functional groups found optimal for binding to iron ore, the backbone of cellulose is constructed of sugars with saturated bonds. Over 30 % of the binder is burnt before 300 ˚C is reached, which is quite stable compared to other organic binders that have been tested *[12]*.

The feedstock used to produce the celluloses affects their properties. Wood, which contains 40-50 % cellulose, gives medium viscosity Na-CMC, whereas cotton, containing 90-99 % cellulose, gives Na-CMC with high viscosity. To achieve low-viscosity cellulose further modifications of wood pulp are needed *[1]*.

Significantly lower dosages of CMC binder are required compared to bentonite in order to achieve the required pellet strengths. Using 0.1 % CMC as binder Bureau of Mines produced green pellets with properties comparable to those with 0.5 % bentonite. However, the values do not quite reach those of pellets with 1 % bentonite. All of the cellulose binders have much higher viscosities and PWAT values compared to bentonite, but the highest PWAT values and viscosity are measured for the purest CMC (CMCH), which had the lowest chloride content.

Adding Na_2CO_3 to CMCH (CMCH0) decreased the viscosity and PWAT value. These values are shown in table 4 *[12]*.

Table 4. Viscosities and PWAT values of bentonite and the different celluloses for 1 and 6 w- % solutions and the aluminium, sodium and chloride contents of the celluloses. Both the PWAT and the viscosities are in distilled water. The code CMCH0 refers to CMCH with 0.03 w-% Na_2CO_3 *[12]*.

Binder	Viscosity (cP) of 1 w-% solutions	Viscosity (cP) of 6 w-% solutions	PWAT	Al content	Na content	Cl content
Bentonite	8	> 150	940	NE	NE	NE
CMCC1	20	> 150	1270	0.8	11.3	8.7
CMCH	90	> 150	3260	< 0.2	7.3	0.2
CMCH0	80	> 150	2150	-	-	-
CMCP1	70	> 150	2550	< 0.2	17.2	9.1

As expected according to the desired binder properties, the pellets produced using the binder with the high PWAT value (CMCH), have the highest drop numbers and compressive strengths (dry and sintered at 1250 ˚C). The comparison between different cellulose grades and bentonite is shown in table below.

Table 5. Cellulose and bentonite viscosities and PWAT values, and the properties of produced pellets. The wet strengths are for pellets at 25 ˚C, dry strengths at 105 ˚C and compressive strengths at 1200 and 1250 ˚C. NE stands for not evaluated *[12]*.

Binder	Dosage (%)	Pellet water (%)	drop number	wet strength (kg/pellet)	dry strength (kg/pellet)	sintered strength (kg/pellet)	
						1200 ˚C	1250 ˚C
Bentonite	0.5	7	4.2	0.73	2.22	77.11	190.51
Bentonite	1	7.6	9.2	1.86	9.48	239.04	334.3
CMCC1	0.1	7.7	3.4	0.95	1.50	207.29	NE
CMCP1	0.1	8.8	5.5	1.50	2.13	115.21	269.89
CMCH	0.1	7.8	3.9	1.09	2.36	NE	316.61
CMCH	0.1	9.0	7.0	1.86	3.18	78.47	305.27

The relatively high drop number and wet strength of pellets with the cellulose containing more sodium carbonate than the others (CMCP1) is due to their higher moisture content. The effect of moisture on these properties can be seen from the results shown in the table for the two batches with CMCH binder but different moisture contents. In addition to this pellets with 0.15 % CMCP1 dosage (8.3 % moisture content) and CMCH (moisture content 8.1 %) had the same drop number of 4.1.

The compressive strength of pellets sintered at 1200 ˚C that are produced with the CMC containing the highest percentage of aluminum and silicon compounds (CMCC1) is nearly double the ones bound CMC with the most sodium carbonate (CMCP1). The value is available

for the CMCH bound pellets chosen for the table. However, the compressive strength of pellets with 9.0 % moisture are only 11 kg/pellet lower after sintering at 1250 ˚C than ones with 7.0 % moisture. The value at 1200 ˚C for the pellets with high moisture content, is 78.47 kg/pellet, which is the lowest of the CMC binders tested. However, when sintered at 1250 ˚C, the compressive strengths are highest. This indicates the CMCH bound pellets needed higher temperature for sintering than the other two binders. This may be due to its purity as it does not have as much of the slag forming constituents as the other CMC binders. The fact that the strength of the CMCP1 bound pellets were significantly weaker than the CMCC1 bound would indicate the silicon and aluminum strengthen the pellet more than sodium.

Several binders based on cellulose and carboxymethyl cellulose have proven to be successful and some even produced commercially. These include Peridur binders developed in 1980s and produced by Akzo Nobel, and Alcotac by Allied Colloids *[12]*. Peridur is a CMC binder and can be prepared by substituting a proportion of hydroxyl groups in cellulose molecules with polar groups to make it water soluble *[5]*.

The Peridur bonded pellets have been reported to have wet strengths comparable to bentonite pellets and better dry strengths. The main disadvantages of Peridur are increased dust formation and the relatively high cost compared to the traditional bentonite. The high cost causes Peridur to be competitive only for concentrates with high silica content that are expensive to refine to meet the specification *[5]*.

6.2 Starches

Starch and cellulose are isomers and thus can be expected to have similar properties. The structural similarity of these polysaccharides can be seen from figure 10 *[5]*. The starches generally contained less sodium than the CMC's, with the exception of the alkalized starch which had 8 % sodium *[12]*. The advantage of starches is they tend to be less expensive than cellulose derivatives. They can be used either dry or "gelled", which refers to starch that has been cooked in water. Starches can be extracted from crops such as corn, potatoes or wheat, and their properties vary depending on the source *[5]*.

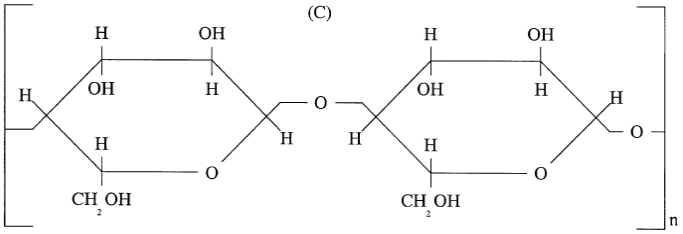


Figure 10. Molecular structure of starch *[5]*.

The backbone of starches is constructed of sugars with saturated bonds, just like cellulose with the main difference in the orientation of the glucosidal bond. Because of this difference, cellulose molecules tend to be highly crystalline *[47]* as they take a linear form with hydrogen bonding between the folds whereas the starch tends to coil into a spiral *[48]*. The hydrogen bonding is the reason for the relatively strong cellulose structure, preventing its dispersion in water *[47]*. Starch is even less stable than cellulose and more than half of the binder been burnt by the time 300 ˚C is reached *[12]*, which may be due to stronger hydrogen bonding.

Based on the molecular structure of an organic binder discussed previously, a modified starch (S-1) with carboxylic and hydroxyl groups was developed by Li *et al. [49]*. The structure of this binder is shown in figure 11. The produced pellets were stronger, especially after drying, than pellets with bentonite binder. The problem with the new binder was that it is rather expensive compared to bentonite *[11]*.

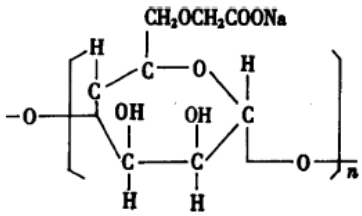


Figure 11. Structure of the modified starch S-1 binder *[11]*.

In a study of organic binders, low viscosity starches (< 75 cP) with PWAT lower less than 100 had very low wet drop values. Alkali starches were found to be the best of the tested low viscosity binders, with highest dry compressive strengths perhaps due to their good adhesive strength. Though the wet, dry and fired pellet compressive strength requirements were met the drop number of pellets was only 4.2. To achieve this drop number, a 0.53 % dosage was required, which is rather high for an organic binder (table 6). None of the other starch binders were tested with dosages this high.

Table 6. Properties of non-gelled and gelled starch binders and their pellets *[12]* and modified starch bound pellets (S-1) *[11]*. NE stands for not evaluated. The drop number for S-1 bound pellets is from 1.0 m height.

Binder	PWAT	viscosity (cP)	Dosage (%)	Pellet water (%)	Drop number	Wet strength (kg/pellet)	Dry strength (kg/pellet)	Compressive strength (kg/pellet)	
								1200 ˚C	1250 ˚C
NG alkalized	520	24	0.25	7.3	3.3	1.09	6.76	173.27	NE
			0.53	7.3	4.2	1.81	15.20	137.44	321.14
SWG70	760	90	0.3	8.4	6.2	1.22	12.97	153.31	331.58
SWG20	870	90	0.1	6.6	4.4	1.50	5.13	201.4	NE
			0.3	7.7	10.4	2.36	18.96	124.28	293.47
SPGC10	850	> 150	0.3	8.3	9.4	1.13	10.43	107.95	307.99
S-1 [11]	NE	NE	0.4	NE	6.7	2.22	32.92	NE	NE

The PWAT value of starches can be increased by using them in the gelled form. The S-1 produced pellets with required drop number, wet and dry strengths, but compressive strengths of sintered pellets are not disclosed. The binders for which the compressive strengths at 1250 ˚C are not disclosed, produces pellets which after sintering at 1200 ˚C have compressive strengths higher than those that have required strength when sintered at 1250 ˚C. Thus all compressive strengths for pellets sintered at 1250 ˚C that are listed in the table below, would be high enough for the industry. The gelled potato and wheat starches reached the required drop numbers with 0.3 % dosages, whereas none of the non-gelled starches gave pellets with drop numbers above 5 at this dosage. These starches had PWAT values higher than 500 and slurry viscosities at the generally used 6 % solids greater than 75 cP *[12]*.

The drop number for 0.1 % SWG20 bound pellets is slightly low, most likely due to the low moisture content. As the dosage is increased to 0.3 %, the drop number increases slightly above the limit to 10.4, partly due to the increased pellet water. The results for alkalized starch shown in the table indicate that sodium may help achieve good final pellet strength. The 0.25 % dosage is lower than most of the other pellets presented in the table. Regardless of this its compressive strengths at 1200 ˚C were the highest. Though it was still below the 250 kg/pellet industry standard, the higher sintering strength may result in the required strength unless the pellets break.

In some floatation circuits the starch is added before filtering the concentrate. In the Bureau of Mines study this was found to increase the moisture content of the pellets and consequently the drop number. However some of the starch was lost in the filtrate, leaving less binder in the pellets. The dry compressive strengths of these pellets were thus lower than perhaps expected *[12]*.

Corn starch has been used as a partial bentonite replacement in doses of approximately 0.05 kg/t (0.005 %). It is composed of amylose and amylopectin in quantities which may vary with the source. Generally the starch is used as such in a pre-gelled form but it could also be easily modified due to reactive hydroxyl groups *[1]*.

6.3 Synthetic copolymers

At Bureau of Mines starch-acrylic copolymers were used as a binder to produce pellets that met the target drop values but had extremely low dry compressive strengths (table 7). As discussed when considering the optimal structure of the organic binder, this is most likely due to the superabsorbent nature of the binder with PWAT exceeding 10, 000 %. The large shrinkage during drying results in large pore size *[12]* and causes the binder tear away from the iron surface *[5]*. The particles being moved apart by the expanding binder may also cause problems in the sintering reactions *[12]*. However the copolymer with the highest PWAT value (PSAGJ in table 7) gave strongest pellets in the group, filling the requirements with 0.20 % of binder. This may be due to its composition as it contained most sodium in the group. The binder in question had the highest sodium content which may explain the better pellet quality.

Table 7. Properties bentonite and starch acrylic polymer binders and their pellets *[12]*. NE stands for not evaluated.

Binder	Viscosity (cP)	PWAT	Dosage (%)	pellet water (%)	Drop number	Wet strength (kg/pellet)	Dry strength (kg/pellet)	Compressive strength (kg/pellet)
Bentonite	60	470	0.5	7	4.2	0.73	2.22	190.51
Bentonite			1	7.6	9.2	1.86	9.48	334.3
PSAGA	> 150	14000	0.5	12.7	5.8	0.45	0.45	118.84
PSAGJ	> 150	50500	0.2	9.2	5	1.27	1.68	275.78

Petrochemical-based polyacrylamide-based binders are anionic and can be prepared by copolymerizing acrylamide and sodium acrylate monomers in a reverse-phase emulsion process or a gel polymerization. The structure of the copolymer in question is shown in figure 12. Because the production process is highly versatile, the polymer can be tailored according to the requirements. The tailoring includes molecular weight, ionic variation and physical form of the polymer. This is a major advantage as plants tend to have different concentrate moisture contents and particle size and their requirements for the pellet strengths may also differ *[1]*.

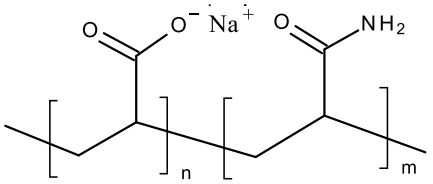


Figure 12. Acrylamide-sodium acrylate copolymer.

The copolymer structure has the carboxyl group which was previously established as the optimal functional group for binding to the iron ore, creating good adhesion. The amide group may also bind to the ore but is not expected to be as ideal. It is also an electron-withdrawing hydrophilic group and thus decreases the affinity of the polar group.

SNF Floerger has produced an anionic polyacrylamide binder called Floform 1049V which was tested in a 120 t/h pelletizing facility. With doses of 0.2 kg/t the pellets fired at 1200 ˚C had compressive strengths higher than 305.91 kg/pellet and their tumbling index was 96.5 %. The total iron content of the fired pellets was increased by 0.3-0.4 % compared to pellets with bentonite binder *[1]*.

The optimum moisture content for pelletization with Floroform was lower than when bentonite was used. This may be due to polyacrylamide distributing the moisture more evenly than the inorganic bentonite. The required low moisture content means the filtration must be done more thoroughly increasing the cost of electric power by 20 %. On the other hand, lower moisture reduces the energy required for drying the pellets. The total energy consumption however may be increased by the replacing bentonite with the organic binder as higher temperatures tend to be needed for the firing of pellets *[1]*.

6.4 Humates

Funa® is a composite matter which consists mainly of humates. It has been patented and is used for commercial production of iron ore pellets for direct reduction and when agglomerating coals and phosphate ores in China. Because Funa is cheaper than several other organic binders, higher dosages can be used *[11]*.

Funa® is made from lignite (brown coal) or weathered coal by extracting a caustic solution *[23]*. In addition to the raw material, pH, temperature as well as liquid to solid ratio affect Funa as a binder. The exact molecular structure of humates is not known but it is believed to

be a highly reactive and amorphous aromatic complex with carboxylic, hydroxyl and phenolic groups. A structure proposed by is shown below and includes all these functionalities *[11]*.

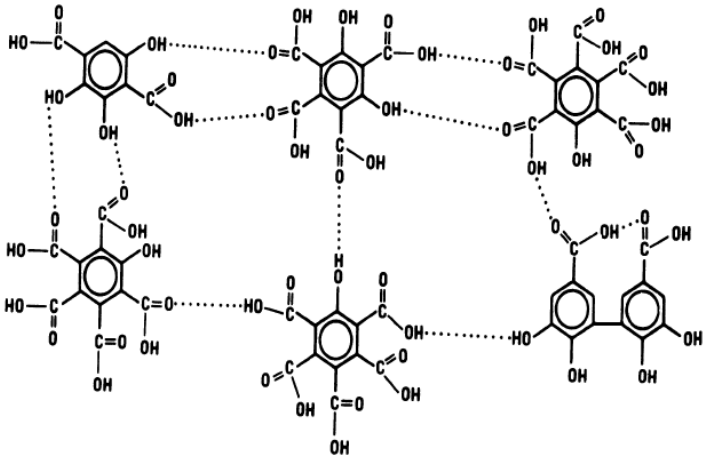


Figure 13. Humate structure proposed by Schnitzer*[50]*.

The carboxylic groups are ideal for binding to the iron ore particle surface, while the hydroxyl groups increase the affinity of the carboxyl groups, its hydrophilicity and thus the iron ore particle ballability, whereas the aromatic ring structure and hydrogen bonding makes it thermally stable. It seems to be a netlike structure with voids, able to trap organic and inorganic compounds such as iron oxides *[23]*. Thus the netlike structure may help retain the water. Humic acids form viscous gels after being treated with a base, usually sodium hydroxide *[1]*. Thus its viscosity can be adjusted in order to affect the pellet properties.

The pellets prepared with Funa have much higher wet and dry strengths than those prepared with bentonite. However, their drop numbers are above 10, thus too high, and the strengths of sintered pellets have not been reported. The dosage could be lowered to get the drop number below the required maximum value, depending on the effect it would have on the compressive strengths of sintered pellets. The results available from the literature are shown in the following table with bentonite values for comparison.

Table 8. Properties of pellets bound with Funa and bentonite *[11]*. NE stands for not evaluated. The drop numbers for Funa *[11]* are from 1.0 m height and 0.5 m height *[1]*.

Binder	Dosage (%)	Moisture (%)	Drop number	Wet strength (kg/pellet)	Dry strength (kg/pellet)
Bentonite	0.5	7.0	4.2	0.73	2.22
Bentonite	1.0	7.6	9.2	1.86	9.48
Funa	1.5	NE	23 *[1]*	2.83	29.25

The adsorption of Funa on magnetite is pH dependent (figure 14). If only small amount of humic acid is added, magnetite can adsorb it entirely (in the figure concentrations up to 0.18 mmol/g). At higher concentrations the adsorbance decreases with increasing pH, because of the more negative oxide surface. The pH dependency of the adsorption is showed in the following figure.

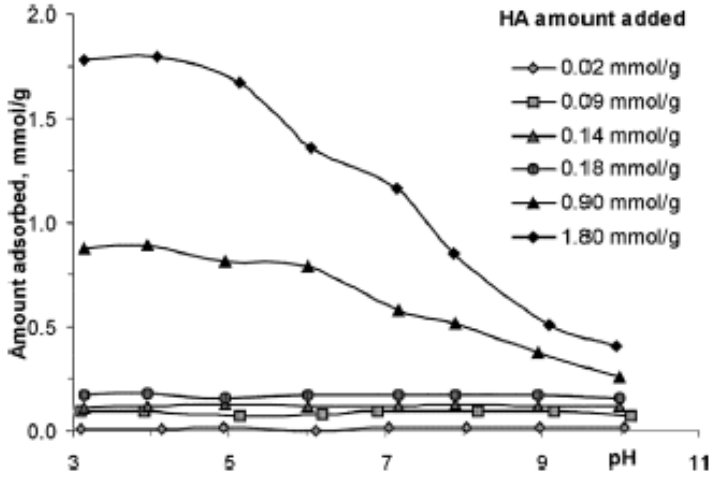


Figure 14. pH dependence of humic acid adsorption on magnetite at different humic acid additions. The amount of humic acid is given in millimoles of acidic group, added to 1 g of magnetite, in the presence of 0.002 mol/l of NaCl at room temperature *[13]*].

When pH is raised from 3 to 4 there is a small increase in the adsorption of humic acid, due to the opposite pH dependency of the humic acid dissociation degree. While the ore has less of the positively charged surface sites at pH 4, there are more of the dissociated anionic acid molecules available for absorption *[13]*].

Qiu *et al.* compared interfacial interactions of Funa with a magnetite concentrate to those of bentonite. Bentonite had little effect on the surface tension, contact angle and wettability and zeta potential of the concentrate indicating poor interaction with the iron ore. In comparison, Funa has been found to possess characteristics of surfactants and colloids, distinctly decreasing surface tension of water. The increase in wetting heat caused by Funa addition was also greater than that of bentonite. The differences between the interaction of the binders can be explained by their molecular structures.

The effect Funa has on the hydrophilic character of iron concentrate and thus its wettability is due to the presence of great number of hydrophilic groups in the humates, which bentonite does not have. The chart a) in figure 15 shows Funa lowers the surface tension significantly

whereas the effect of bentonite is quite insignificant. From chart b) the same effect can be seen for the contact angle *[23]*.

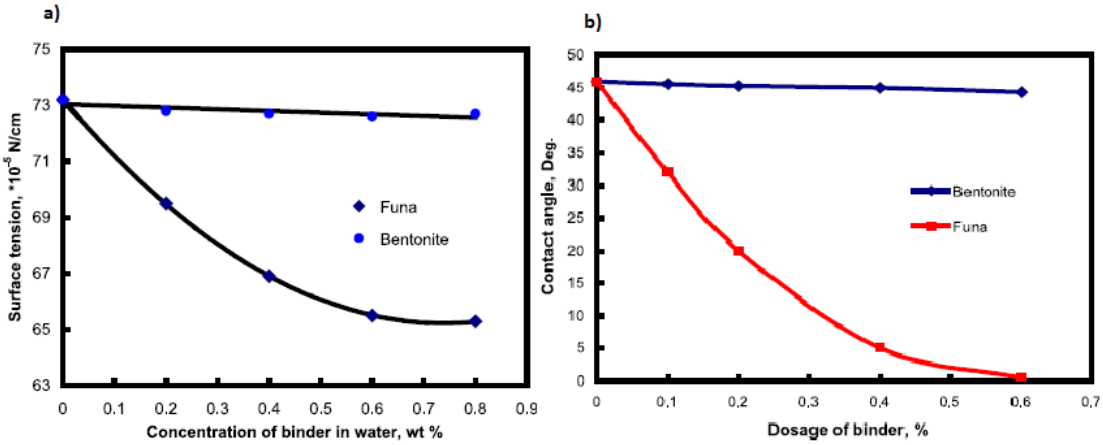


Figure 15. a) Effects of binder dosage on the surface tension and b) contact angle *[23]*.

Funa lowers the contact angle of magnetic concentrates from 46˚ to nearly 0˚ at a 0.6 % dosage by making the concentrate more hydrophilic. This effect is due to the hydrophilic groups in its molecular structure of Funa which affect the ore properties when chemically adsorbed on the surface *[23]*. Lowering the surface tension means the binder liquid behaves like a surfactant and spreads on the concentrate. However, it disfavors the wetting of the ore particles by reducing the driving force of penetration between the ore particles (equation 2) *[11]*.

The iron ore concentrate studied by Qui *et al.* had a zero charge point at pH 4.4 and a zeta potential of -10.5 mV at neutral (approximately pH 7), indicating the particles do not have high repulsion and can be agglomerated. Chart a) in figure 16 shows that the zeta potential of bentonite is lower than that of the concentrate, but within the pH range they are both within the binding region of the zeta potential. *[25]* From chart b) it is apparent that Funa lowers the zeta potential of the concentrate much more than bentonite and the effect increases significantly with the binder dosage *[23]*.

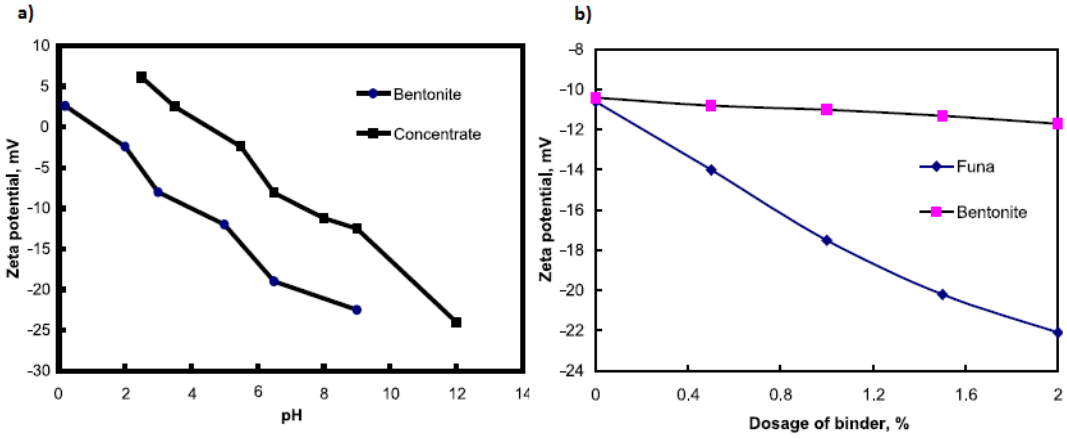


Figure 16. Effect of a) pH on surface electrical properties of the concentrate and bentonite and b) binder dosage on the zeta potential of iron concentrate *[23]*.

Due to carboxyl groups in its structure Funa is dissociated into negatively charged ions in water which are chemically adsorbed on the oxide surface. In small amounts the humic acid neutralizes the positive surface charge significantly, decreasing the colloidal stability of magnetite *[13]*]. However, at high humic acid concentrations, the Funa coated ore particles become negatively charged due to excess acidic groups of the polyanion which cannot bind to the surface due to steric reasons *[24]*. Thus the zeta potential of the concentrate becomes more negative with added Funa re-stabilizing the colloidal magnetite by increasing the repulsion between the particles with the same charge. This means Funa further increases the repulsion between ore particles, hence other significant interactions are needed to adhere them together than electrostatic *[23]*.

6.5 Gums

The guar gums are derived from guar beans and consist mainly of nonionic, high molecular weight polysaccharides and proteins *[1]*. The cost of gums is greatly affected by competition for the material and cost of shipping. This is why there is more interest in using guar gums as binders near the areas where they are grown *[5]*, such as India, Pakistan, Texas and Oklahoma *[1]*.

Guar gum forms extremely viscous, colloidal dispersion at very low doses, making it attractive for pelletization as high viscosity tends to produce good results *[1]*. They have been found to be most effective with higher moisture contents, consequently producing pellets with high

drop numbers *[12]*. The guar gum structure is similar to starch and can be easily modified *[1]*, enabling binder tailoring into a wide range of products.

The Jaguar gums are high-molecular-weight materials composed of straight-chained mannan, branched at regular intervals with galactose units on alternate mannose units *[5]*. This material has several of the characteristics of an optimal organic binder (figure 17): high molecular weight and branched structure as well as hydrophilic hydroxyl groups.

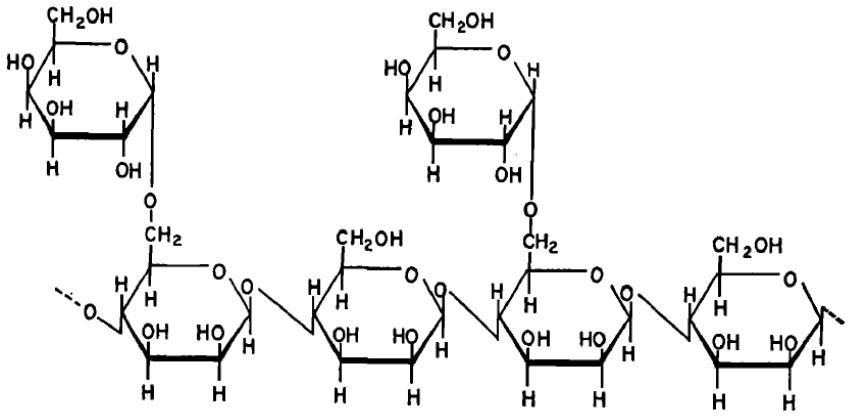


Figure 17. structure of "jaguar" guar gum *[51]*.

However, hydroxyl groups are the only substituent in the jaguar. Thus unlike the modified starches and cellulose, it does not have the ionic COO^- group. Thus the less optimal hydroxyl groups are responsible for both binding to the ore particles and making it wettable. As the guar gums can be easily modified like starch, some of the hydroxyl groups could be turned into the anionic COO^- groups that have proven effective in cellulose (Na-CMC) and starches (S-1).

Several varieties of "Jaguar" guar gums have turned out to be promising binders. The most suitable varieties of Jaguar tend to be the ones with highest viscosities, indicating high viscosity as a desired characteristic for organic binders *[12]*. Properties of pellets produced with a variety of natural gums are shown in table 9.

Table 9. Properties of bentonite and natural guar gum binders and their pellets *[12]*. The viscosities are for 6 w-% solutions and NE stands for not evaluated.

Binder	Dosage (%)	Moisture (%)	Viscosity (cP)	PWAT	Drop number	Wet strength (kg/pellet)	Dry strength (kg/pellet)	Compressive strength (kg/pellet)	
								1200 ˚C	1250 ˚C
Bentonite	0.5	7.0	60	470	4.2	0.73	2.22	77.11	190.51
Bentonite	1.0	7.6			9.2	1.86	9.48	239.04	334.3
GG211	0.1	9.7	> 150	1030	11.9	1.27	2.6762	112.94	292.11
GG211D	0.1	8.7	> 150	900	6.1	1.13	2.7669	91.17	207.29
GG416	0.1	7.9	> 150	1850	8.2	2.22	2.5855	136.53	300.28
GX	0.1	7.8	> 150	4890	3.4	1.09	1.9051	158.76	NE

The GG416 was the only gum to produce pellets with required physical properties as GG211 bound pellets were too elastic with drop numbers above 10, while GX bound pellets had drop numbers below 5 and GG211D bound pellets had sintered strengths below 250 kg/pellet. Both the guar gums (GG) and xanthan gum (GX) had lower sodium content than the CMC's. GX had the highest salt content (Na and K) and most impurities of the natural gums. The GX had the lowest viscosity with 120 cP at 1 w-% solutions while the other gums had viscosities above 150 cP even at the low viscosity. It produced pellets with lowest drop numbers and highest compressive strengths of the pellets bound with natural gums when sintered at 1200 ˚C. However their compressive strengths were not evaluated at 1250 ˚C. The strengths of sintered pellets increase with increasing PWAT value even though it would be expected increase the porosity.

6.6 Tars and bitumens

Bitumen is a low-cost heavy hydrocarbon available in naturally occurring forms and oil refining residues. It is very adhesive and hardens when losing volatiles at relatively low temperatures *[5]*. Bitumen is however highly viscous and hydrophobic, which makes it hard to mix into the iron concentrate. Hence it has been used mainly in briquettes, although wetting agents could help when pelletizing with bitumen *[1]*.

Water soluble sulfonated pitch has also been tried for iron ore pelletizing. In further investigations however the pitch bound wet balls properties were found noticeably inferior to bentonite iron ore pellets although the dry compressive strengths were similar or in some cases even superior. The preheating strengths of pitch pellets were also inferior to the ones made with bentonite, most likely due to the pitch burning away *[5]*.

6.7 Organic waste

Several waste products from food and paper industry have binding properties. However, it is difficult to achieve consistent performance with waste as its properties are not controlled. Many waste products with binding properties such as food and dairy wastes, municipal sewage and paper mill sludges are slurries which decompose rapidly and produce smell. Reducing this problem by drying the material or adding a biocide would increase cost diminishing the advantage of waste being available at low cost *[5]*.

Some food wastes, such as lactose whey and whey permeate, are sticky which is an indication of binding properties *[5]*. However, pellets made using this type of binders did not perform well largely due to their negative PWAT values, indicating they were partly dissolved and lost during the adsorption tests *[12]*.

Paper mill sludges are rich in wood fibers and contain also clays and organic chemical. Clays are not burnt away completely but on the other hand they may bind the particles until the pellets reach the sintering temperature. Raw sludges had low PWAT values mainly due to their high water content *[5]*. To produce pellets of good physical quality, approximately double the dry-equivalent weight of sludges was needed compared to bentonite *[1]*. The pellets had superior metallurgical properties compared to bentonite pellets but the quality of green balls and fired pellets was poorer *[5]*. The raw sludges are difficult to mix with the concentrate while keeping the optimal moisture level *[1]*.

To be a practical binder, the sludge would need to be dried and ground which would increase the cost. However, it would be less effective as a binder because dried sludge does not rehydrate readily *[5]*. The clays in the sludge contain silicon and aluminum just like the bentonite. The levels of these contaminants were found to be in the same range as in pellets pelletized with 0.5-1 % bentonite *[1]*. As the main reason for researching organic binders was to reduce the silica content, the sludges from paper mills are not potential substitutes for bentonite.

Spent sulphite liquor is also a by-product of paper mills. It gives pellets with similar properties to bentonite pellets but is very high in sulfur, which is an undesirable contaminant for the blast furnace feed and thus not discussed further *[5]*.

Peat moss consists of partially decomposed vegetation making it similar to the paper mill sludges. The pellets produced using the gel from peat moss, were reasonably high-quality. However, it is obtained from bogs that reproduce slowly making it environmentally questionable *[5]*.

Municipal wastes are also similar to that from paper mills but the composition is more varied with a lower fiber content and higher colloidal and undesirable contaminant (particularly phosphorus) concentration *[5]*.

7. Chemical additives

Interactions between binders and the iron ore are largely controlled by the charge density of the mineral surface, and adsorption of different species. Surface charge density and wettability can be altered by the pH of the process water. Chemicals used at previous stages of iron ore processing, such as flotation chemicals, can affect the functioning of the binder and the pelletizing process. However, this means also that additives can be used to enhance the interaction of the ore towards the binder. In order to enable efficient balling and high strength of pellets, the surface of iron ore needs to be sufficiently hydrophilic after flotation. Contamination of the iron oxide with flotation collection chemicals, such as anionic polymers, turn it hydrophobic and may cause inclusion of air bubbles inside the green pellets during wet agglomeration, resulting in weak pellets. Sodium silicate could protect the iron oxide surface from collector absorption, but would contaminate the pellets like bentonite. Calcium ions present in the process water promote undesired precipitation and adsorption on the mineral surface, even in the presence of silicate *[37]*.

Water used in the iron ore manufacturing process contains significant concentrations of dissolved solids with calcium, sodium, potassium and magnesium, sulfate and chloride as the main components. Especially divalent cations such as calcium and magnesium are adsorbed onto the iron concentrate and transported to the agglomeration process ending up in the final product *[52]*. According to Ripke and Kawatra this is due to the concentrate surface being negatively charged which attracts positive ions. This results in an electric double layer with large excess of positive ions over negative ions adjacent to the surface. Due to the attractive forces ions remain attached to the particle surface while the bulk of the water is removed in the plant filters. Multivalent ions are more strongly influenced by this effect than

the monovalent ions resulting in higher calcium and magnesium concentration *[53]*. This phenomenon results in Ca^{2+} and Mg^{2+} levels being up to 500 times higher than had been expected from analyzing the plant recycle water (table 10).

Table 10. Ionic concentration of water samples from an iron ore concentrator located in the Lake Superior district of the United States. The tap water used for comparison is a sample of Houghton, Michigan. All the values are in mg/l (ppm) *[53]*.

Ion	Magnetite concentrate moisture (undiluted) (mg/l)	Plant filtrate water (mg/l)	Tap water (mg/l)
Calcium	5088	9.3	39.6
Magnesium	5995	14.7	9.3
Potassium	1680	10.8	1.7
Sodium	725	151.0	17.3
Sulfate	803	54.0	21.0

As it can be seen from the table above, the concentrations of monovalent ions can be close to 1000 mg/l in pellet moisture, whereas concentrations of divalent ions can be as high as 5000 mg/l. The water extracted from the magnetite filter cake had concentrations of Ca^{2+} and Mg^{2+} 550 and 400 times higher than the filtrate water recycled to the plant. The sulfate is also much more concentrated in the pellet moisture than in the recycle water, even though the ion is negatively charged and would thus be expected to have repulsive interaction towards the concentrate. The cations were released from the surface by rinsing the concentrated with distilled water at pH 5.5. This changed the concentrate surface charge from negative to positive *[53]* thus switching the attraction between the cations and the anions to repulsive.

Gotzman *et al.* have found washing concentrates (Evtac and Minntac mines from Minnesota) to improve their agglomeration with CMC binder and the quality of green pellets. Allen reported similar improvements in agglomerating washed iron ore concentrates with Alcotac anionic polyacrylamide binders. The green pellet quality is improved also by moistening it with water softened by adding either carbon dioxide or sodium carbonate. The softened water causes Ca^{2+} ions are precipitated as $CaCO_3$, decreasing their concentration. Furthermore, increasing the green ball moisture Ca^{2+} concentration from 0 to 208 ppm reduces the wet drop number from 5.6 to 5.0, wet compression strength from 1.4 to 1.2 kg/pellet and dry compression strength from 1.8 to 1.2 kg/pellet. Both findings suggest that Ca^{2+} ions have a harmful impact on the pellet properties *[1]*.

The cations have negative effect on pelletization with bentonite *[53]* and possibly with some organic binders *[1]* as well, such as CMC. Water soluble anionic polyacrylamide and CMC binders tend to be monovalent cations, such as sodium. These binder molecules unravel and extend when in moisture, due to ionic repulsive forces from the charged groups (generally COO^-). Divalent cations, such as Ca^{2+}, may shield those repulsive forces. This would prevent the molecules extending into the liquid, causing them to stay more coiled and hence decreasing the pellet moisture viscosity. This means ionically charged organic binders are sensitive to water chemistry. Due to these findings organic binders are often used with an inorganic additive such as sodium carbonate, which precipitates calcium and magnesium out of solutions as their carbonates are less soluble *[1]*.

As organic binders are burnt in lower temperatures, the pellets lack slag film bonding. The resulting poor compressive strengths can be enhanced by using additives, such as boron minerals *[8, 17]*, sodium carbonate or chelating agents and dispersants *[1]*.

7.1 Sodium carbonate and sodium chloride

Sodium carbonate, also known as soda ash, is commonly added to Na-CMC and anionic polyacrylamide binders in order to precipitate the divalent calcium and magnesium ions, i.e. softening the water and to speed the dissolution and dispersion of binders. It is generally added as a dry powder either separate or mixed with the organic binder. Sodium carbonate quantities can make up to 50 % of the total binder weight, varying with both ore and process conditions. When used with Alcotac binder, sodium carbonate increased the pellet water content and made it more stable. This may explain the improved green ball quality mentioned previously *[1]*.

Haas *et al.* found that highest fired pellet strengths were generally achieved with binders that contained most alkalis (Na^+ and K^+). They believed this was due to the low melting points of the alkali compounds *[12]*, which would add to the slag phase.

A small improvement in drop number and compressive strengths of pellets were obtained, in the Bureau of Mines study with, 0.03 % addition of Na_2CO_3 or NaCl to 0.15 % of the CMCH binder (coded as 0.18 % CMCHO and CMCHL in table 11). However, adding both Na_2CO_3 and NaCl (0.21 % CMCHOL) together did not further improve the pellet quality, but instead seemed to lower it slightly compared to the pellets with only one of the additives. Doubling

the carbonate dosage to 0.06 % and adding it to the concentrate with 0.15 % of the CMCH (coded CMCHOO) gave too high drop numbers indicating the pellets would be elastic and turn into ovals under pressure. Increasing the carbonate dosage from 0.03 % to 0.06 % slightly decreased while increasing the compressive strengths of wet and dry pellets, decreased the sintered strength *[12]*.

Table 11. Effect of Na_2CO_3 and NaCl on pellet properties *[12]*.

binder	dosage (%)	pellet water (%)	drop number	wet strength (kg/pellet)	dry strength (kg/pellet)	Sintered strength (kg/pellet)
CMCH	0.15	8.1	4.1	1.04	5.72	267.62
CMCHL	0.18	8.1	6.6	1.41	6.12	318.88
CMCHO	0.18	8.2	5.5	1.32	6.99	316.15
CMCHOL	0.21	8.3	5.3	1.22	4.99	309.35
CMCHOO	0.21	8.9	14.7	1.36	8.85	293.02

Whistler on the other hand found that NaCl decreases wet drop and dry strength when used with high molecular weight Na-CMC and negligible effects on binders with lower molecular weight. Salt is known to inhibit the expansion and dissolution of Na-CMC *[41]*. This explains the lowered viscosity of CMCH when Na_2CO_3 is added and may be the reason for increased pellet quality when salts. The higher molecular weight binders would already dissolve less readily causing the effect of NaCl to be more profound *[11]*. However, there were no results available on this study.

Ore concentrates, such as hematite ores from Brazil, Venezuela and Canada, that have been difficult to pelletize with the traditional binders can be agglomerated with mixtures of Na-CMC and soda ash with varying amounts of sodium citrate (0.005-0.1 %) and sodium hydroxide (0.005-0.05 %). These combinations are believed to make the zeta potential of the ore concentrate more negative and limit the deactivation of the Na-CMC binder.

7.2 Boron-containing compounds

Natural borate minerals have been agglomerated with iron ore concentrate in order to increase the strengths of preheated and fired pellets. They have low melting temperatures, which promote the sintering of iron ore grains and form an additional slag-bonding phase to the pellet *[1]*. Colemanite has been found to be the most potential of the borate minerals. It is a Ca-borate salt, $2CaO_3B_2O_3{\cdot}5H_2O$ *[8]*, with melting point at 986 °C*[42]*. This is significantly lower than for bentonite which starts to melt at 1200 °C *[29]*. The colemanite was also found

to reduce the melting temperature of silicon dioxide (SiO_2). Thus both the binder and the silica from the concentrate start slag bonding earlier than with bentonite.

A typical colemanite sample chemical composition is 41.00-43.00 % of boron trioxide (B_2O_3), 26.00-28.00 % of calcium oxide (CaO), less than 6.50 % of silica (SiO_2) and 0.50 % sulphur trioxide (SO_3). Thus its silica and alumina contents are significantly lower than those of bentonite, which tends to contain about 60 % silica *[8, 29]*.

According to Sivrikaya *[29]*, adding 0.50 to 1.00 % of boron minerals such as colemanite into agglomeration feed caused pellets to spall after thermal treatment. He explained this observation by the decrepitation of boron minerals due to the considerable amount of water chemically bonded to their structure. Therefore, the chemically bonded water should be removed from boron compounds before their use in iron ore pellet production. This is referred to as pre-calcination.

According to Sivrikaya and Arol, while organic binders tend to produce good quality green and dry pellets, the pre-heated and fired pellets often fail to achieve the required compressive strengths *[31]*. On the other hand colemanite provides required pre-heated and fired pellet strengths but the wet and dry pellet qualities are insufficient *[8]*. Colemanite bound pellets are very fragile, with drop numbers equal to ones with no binder. The drop numbers of bentonite bound pellets are also slightly below the industrial minimum level of 5 (figure 18), but bentonite is commonly used as a reference. These trends can be seen from the following figures.

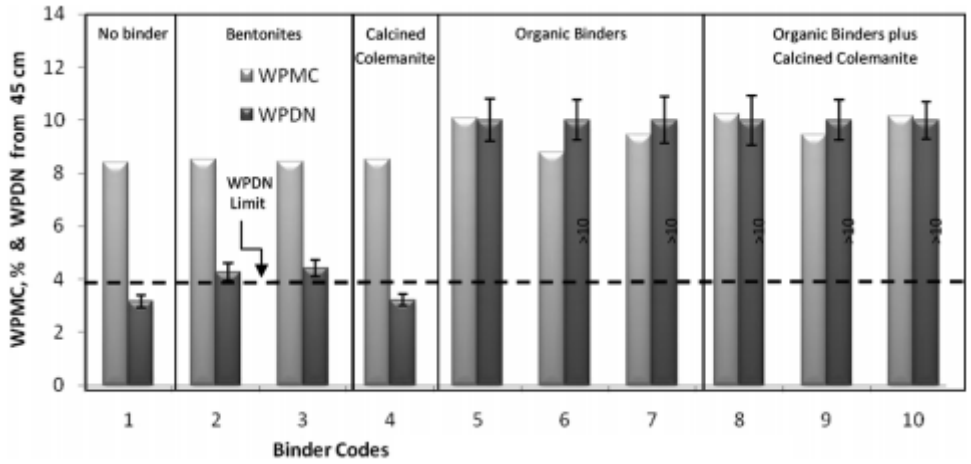


Figure 18. Wet pellet moisture content (WPMC) and drop numbers (WPDN) obtained with different binders. The mean values are given with the 95 % confidence interval. Binder codes: 2 0.6 % bentonite with higher silica content, 3 0.6 % bentonite with lower silica content, 4 0.66 % calcined colemanite, 5 0.10 % technical CMC, 6 0.10 % DPEP06-0007 Polymer, 7 0.10 % superfloc A150-LMW. Binder codes 8-9 refer to the organic binders in the same order but with 0.66 % calcined colemanite *[8]*.

The dashed line at 4 was the target value determined in the article. However, it is too low for the industrial requirements. The CMC used to obtain the figure above, is a derivative of cellulose and is commercially available. The DPEP06-0007 polymer is an anionic copolymer blend supplied by Ciba®. The drop numbers of pellets with organic binder either by itself or with colemanite are significantly higher, at the industrial maximum for drop numbers. The colemanite does not affect the drop number values which explains the similar values between pellets with calcined colemanite binder and no binder.

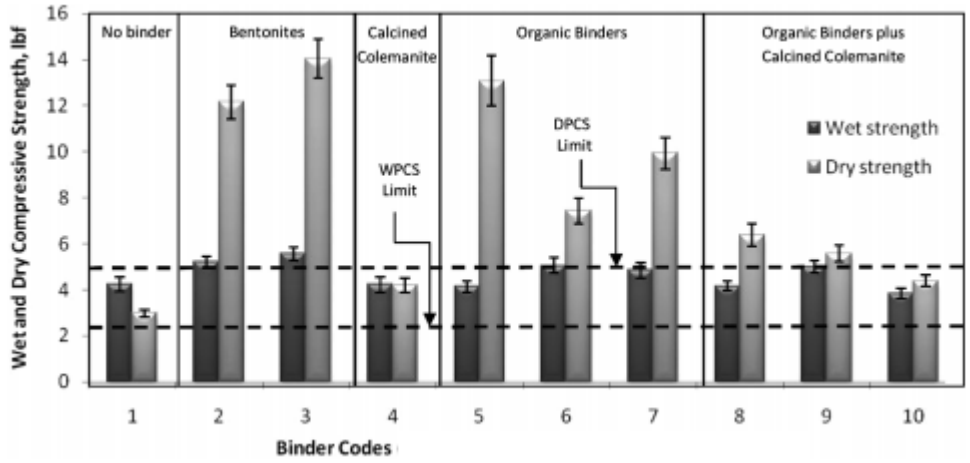


Figure 19. Compressive strengths of wet (WPCS) and dry (DPCS) pellets obtained with different binders. The mean values are given with the 95 % confidence interval. Dashed lines show 2.2 lbf (1 kg) and 5 lbf (2.2 kg) which is the required minimum limit for wet and dry pellets *[8]*.

Calcined colemanite produces pellets with required wet pellet strength but poor dry pellet compressive strengths. The values are close to those of pellets produced with no binder.

Organic binders on the other hand exceed the required values. The CMC binder produce pellets with values similar to bentonites. Adding calcined colemanite together with organic binders to pellets improve their sintered strengths but decrease the dry strengths.

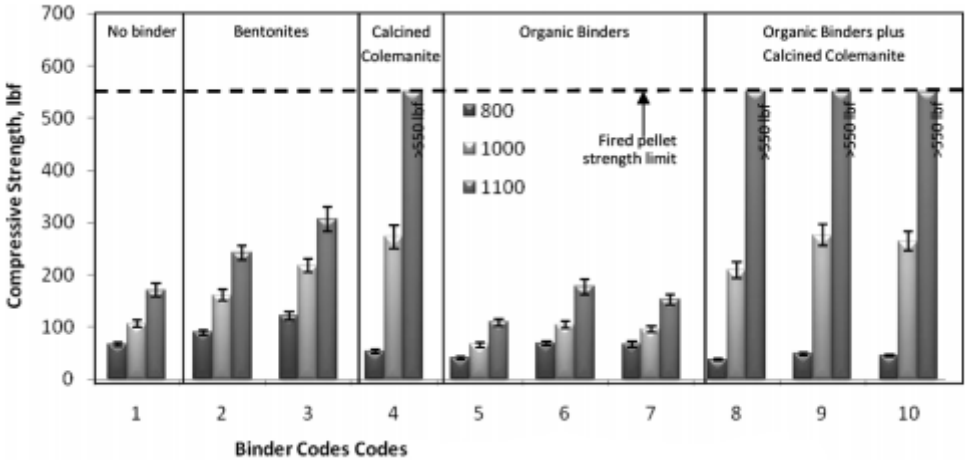


Figure 20. Compressive strengths of thermally treated pellets (800, 1000, 1100) with different binders. The mean values are given with the 95 % confidence interval. Dashed line shows 550 lbf, which is the industrially desired minimum strength of fired pellets (250 kg) *[8]*.

Adding colemanite with most organic binders gives significantly better pellet sintered strengths, while only slightly decreasing the dry strengths. Thus the organic binder should give the pellets exceptionally good dry strength, hence allowing for use of calcined colemanite as an additive to improve the sintered strength. As the industrially sufficient compressive strengths were achieved already at 1100 °C, lower sintering temperatures compared to the currently used 1250-1350 °C *[8]* would be enough. This would mean energy savings and increased reduction rates, as increasing the sintering temperature tends to decrease the reducibility *[12]*.

Pellets produced with calcined colemanite from magnetite concentrate have higher sintered strengths than the ones from hematite concentrate. However, the opposite was observed for bentonite. Kawatra and Halt reported similar results for bentonite bound pellets. They concluded particle size was not the dominant contributor and suggested the cause may be mineralogy, such as particle shape, and presence of residual reagents from the concentrator *[6]*. Thus the calcined colemanite would be more useful for agglomerating magnetite concentrates than hematite concentrates.

Sivrikaya and Arol reported the metallurgical and chemical quality of pellets produced using combined binders to be good compared with bentonite-bonded pellets used as a reference.

According to their study, organic binders and boron compounds did not contaminate the pellets and thus would not interfere with iron production *[54]*. On the other hand when B_2O_3 content was increased to a high 2.0 % strength of sintered pellets and degree of reduction decreased. The increase in boron compounds results in decreased porosity due to the higher slag mineral quantity *[1]*.

However, the table does not show the boron content of pellets, or consider how the boron left in the pellets would affect the later steps of iron and steel production. Boron dissolves in pig iron, reducing the quality of iron and steel *[55]*. It has been suggested that pellets agglomerated with borate minerals could be used to produce boron-alloyed steels *[1]*. However, even in boron steel wires the boron concentration is extremely low, between 0.0005 and 0.0030 %. This is because boron causes brittleness even in concentrations as low as 0.0010 % and susceptibility to welding cracks *[55]*. Thus the amounts of boron that can be added in the binder without removing it from the final product would be extremely low. Thus efficient methods would be needed to remove the boron in order to make its use viable.

According to Sato et al. the conditions favouring removal of boron are the same as those of dephosphorization: low temperatures, a high basicity of slag, and a high oxidation atmosphere *[55]*. Therefore, if dephophorization is required, boron could be removed simultaneously.

7.3 Chelating agents and dispersants

A chelate is used for coordination or complex compounds consisting of a central metal atom attached to a large molecule, called a ligand, with two or more separate coordinate bonds forming a cyclic *[56]*. A chelating agents are generally organic molecules with at least two sites that can coordinate to a metal *[57]*. Dispersing agents, also known as dispersants, added to suspension to enhance separation of particles preventing them from clumping. They are generally fairly low-molecular-weight materials that strongly adsorb onto particles forming a repulsive barrier to the positive forces of interaction that exist between all particulate materials *[58]*.

Several chelating agents and dispersants have been found to improve the binding characteristics of certain organic binders. These include citric acid, sodium tripolyphosphate (TPP) and sodium hexametaphophate (SHMP). They may sequester elements in the

agglomeration feed that are harmful for pelletizing, such as calcium and magnesium. This may improve the dispersion of organic binders into the green-ball moisture, preventing their excessive precipitation or adsorption onto particle surfaces *[1]*. The structures of the additives are shown in the figure below.

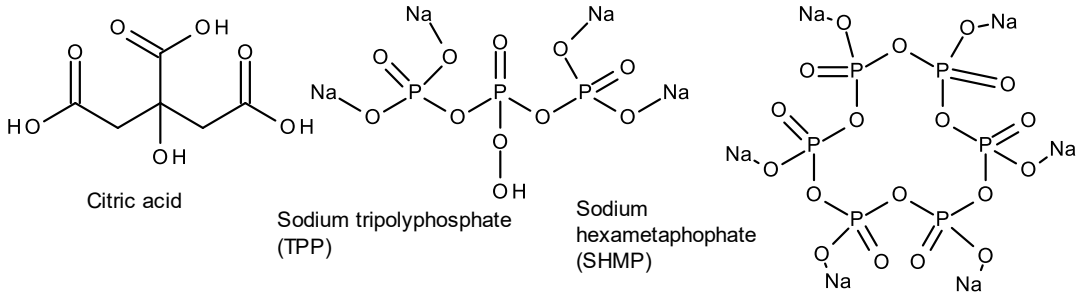


Figure 21. Structures of chelating agents and dispersants used as additives for iron ore agglomeration *[1]*.

Citric acid has three acidic groups and TPP and SHMP have several ionic bonds between oxygen and sodium, giving them high anionic charge. Due to the high charge they bind to calcium and magnesium dications tightly so that they do not interfere with the organic binders.

Citric acid, which functions as a chelating agent, can be added as a sodium salt to anionic polymers such as CMC. The doses are usually between 45 and 90 mg per ton of feed. This is quite high for an additive as organic binder dosages tend to be in similar rage. SHMP a common dispersant and can make up to 50 % by weight of the organic binder *[1]*.

Sodium tripolyphosphate (TPP) is a common dispersant that also functions as a chelating agent. An organic binder can contain 30-50 % by weight of TPP *[1]*. De Moraes *et al.* reported the CMC bound pellets to demand large amount of water for pelletizing, which would increase the weight of the pellet bed causing them to deform. TPP was found to decrease the required moisture *[7]*. The effects of the dispersant on CMC are shown in the table below and compared with bentonite bound pellets.

Table 12. Effect of the dispersant sodium tripolyphosphate (TPP] on the strength of CMC-bonded pellets *[59]*.

Binder	Dose (%)	Moisture (%)	Wet drop	Compressive strength (kg/pellet)		
				Wet	Dry	900 °C
Bentonite	0.66	9.5	3.2	1.94	3.91	12.23
CMC	0.04	8.9	2.4	1.72	1.62	5.22
CMC + TPP	0.04 + 0.02	9.1	2.9	2.03	2.19	9.11

From the figures it is evident that TPP improved the compressive strengths of CMC bound wet, dry and pre-heated pellets. Values similar to the bentonite reference pellets are however reached only for the wet pellets. The higher drop numbers of the pellets with TPP and bentonite bound pellets are at least partially due to the higher moisture content. This contradicts the reported effect of TPP lowering the required water required for pellet production. However de Moraes refers to tests conducted by Cassola and Chives that indicate TPP would be more effective alone than with CMC *[7]*.

8. Potential organic binders

Difference in material (moisture content, sizing et.) and the lack of standard method for pelletizing makes it more difficult to compare binders tested in different laboratories.

Na-CMC and copolymers of acrylamide and sodium acrylate which have both been successful on an industrial scale have only single bonds in their backbone structure. The same applies for anionic polyacrylamide and starches that have been studied extensively and have shown some promising results. Making similar structures to these but adding double bonds and aromatic rings to improve their thermal stability whould perhaps enhance the pellet properties. However, this type of structures tends to be quite expensive. The thermal stability of the binders is not taken into consideration when choosing them for testing, as the poor compressive strengths of sintered pellets can be compensated using additives, such as $NaCO_3$ or perhaps calcinated colemanite.

The idea of superabsorbent as the binder was considered but as stated previously binders with extremely high absorbability such as starch acrylic copolymers (PWAT > 10 000) tend to result in weak dry and fired pellets. Thus most likely it would not be suitable for a binder by itself. It could perhaps be used together with other organic binders to absorb extra moisture from the ore concentrate to achieve drier surfaces and help control the balling rates.

8.1. Polyacrylic acid

Several polyacrylamides and acrylamide copolymerized with sodium acrylate or acrylic acid have been found to produce pellets that meet the quality specifications. Carboxylic acid would theoretically interact better with the iron ore than an amide as it is more anionic thus adsorbing better on the positive iron oxide. No reports on polyacrylic acids for pelletizing iron ore were found. The binders with acid groups were generally modified CMC binders. Either reducing some of the acid groups of a polyacrylic acid or changing them for an hydroxide group could enhance the affinity of the carboxyl group towards the iron ore. This would theoretically increase the affinity of the acid group by increasing its electron density.

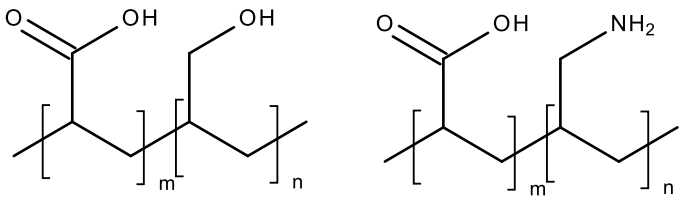


Figure 22. Interesting binder structures.

Polyacrylic acids can be prepared by hydrolysing polyacrylamide. The degree of substitution can be controlled to some extent with the strength of the base *[60]*. However, high and low degrees of substitution may be difficult to achieve. Another option is to take large polymers with the right anionic charge and break them up by adding peroxide during intense mixing. Changing some of the groups into hydroxyl groups could make the binder more optimal but it may be unreliable and would add a variable to the results. By pelletising with binders with different degrees of hydrolysation the efficiency and benefit of the anionic carboxyl group can be studied.

8.2. Silane

Silane had not been reported as an binder for iron ore pelletisation but had been used as an adhesive between organic and inorganic materials for several applications *[19]*. Organofunctional silanes have been used for corrosion protection of metals *[61]* and as adhesives between organic and inorganic materials for example in composites used in the automotive, aerospace and electronics markets *[19]*. The silicon compounds tend to form a covalent bond with hydroxide groups of metal oxides and other inorganic materials *[62]*. This makes the silanes an interesting possibility for a binder or an additive with a polymer. However, the silanes tend to be hydrophobic, which may cause problems during the palletization.

Mono-silanes were chosen for the study as they are available from Wacker with a general structure of $X_3Si(CH_2)_nY$, where Y represents an organofunctional group such as carboxylic acid, amide or amine and X represents a silicon ester *[62]* such as methoxy or ethoxy, which can react with various types of hydroxyl groups liberating methanol or ethanol as a side product *[61]*. Typically, the length of the carbon chain (value n) is about 3. Both the Y group type the chain length n influence the water solubility of the monomer *[62]*.

Before application on any substrate silanes need to be hydrolyzed to form silanol Si-OH groups that can interact with each other and the metal through condensation. The silanes are usually applied as dilute water solutions where the hydrolyzation reaction, catalyzed by acid or base, takes place (figure 23).

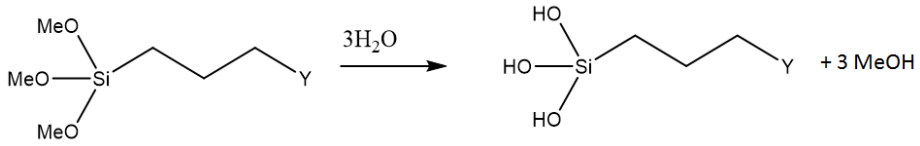


Figure 23. Hydrolysis of the silicon ester *[62]*.

The kinetics and equilibrium of the hydrolysis reaction depends on the nature of the organofunctional groups, silane concentration, temperature, pH and aging of the solution. As the reaction can be catalyzed by either acid or base, the pH has a major impact on the reaction *[62]*.

After hydrolysis, the formed silanol groups can undergo condensation reactions resulting in polymerization and binding to the metal. The silanol groups are first adsorbed on the metal through hydrogen bonding. During drying or curing the SiOH groups and M-OH groups go through condensation forming metallo-siloxane (ME-O-Si):

$$Si - OH + HO - Si \leftrightarrow Me - O - Si + H_2O \qquad (1)$$

Simultaneously to condensation with the metal the silanol groups (SiOH) react with each other crosslinking through condensation reactions to form an Si-O-Si network *[62]*[y]:

$$Si - OH + HO - Si \leftrightarrow Si - O - Si + H_2O \qquad (2)$$

The wet pellets are held together by capillary forces while wet and as these forces are weakened during drying at 105˚C *[1]*, the condensation reactions should start strengthening the pellets. The reversibility of the reactions should not be a problem if the sintering is done soon after drying, before the pellets start to adsorb some moisture from the air. The entire process is shown in the following figure.

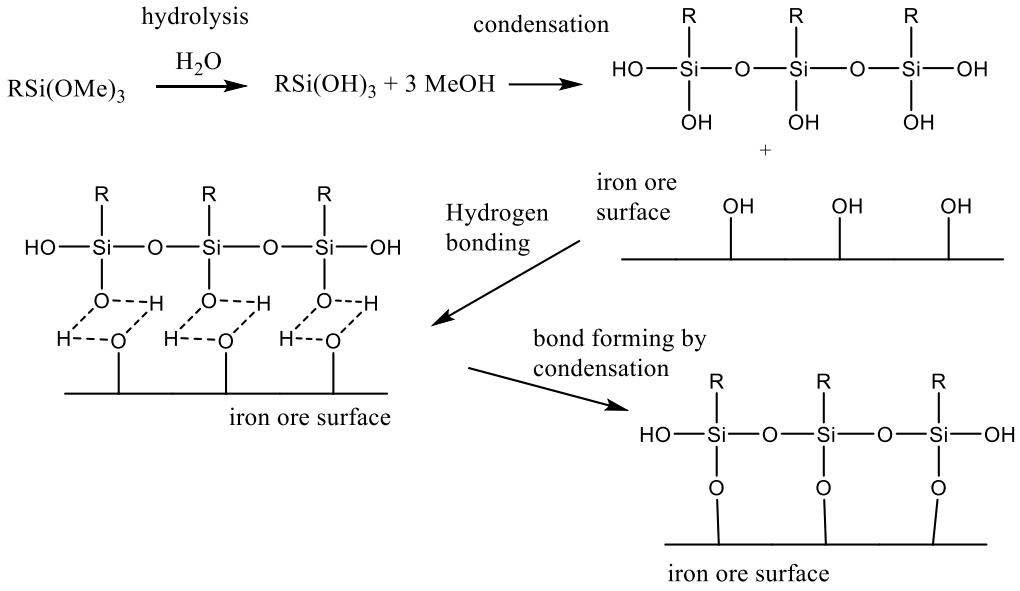


Figure 24. Forming the SiOSi network and metallo-siloxane bond formation *[61]*.

For some metals such as aluminium there is little doubt the covalent bonds are formed. However the bond is expected to be less stable for iron than for aluminium *[45, 63]* and according to some research may not even proceed beyond hydrogen bonding *[62]*. Nazarov et al. claimed that stable ferrosiloxane bonds were formed on iron in borate solutions with pH 8.5 *[64]*. If the formed bond would be covalent, it would be stronger than hydrogen and anionic bonding that the functionality of most organic binders is based on. However, the pelletizations are performed with water rather than borate solutions. Organosilanes have not been used for iron ore pelletisation before. Hence it is difficult to say whether the silanol groups will be able to create a sufficient network at the low binder dosages to reach high molar mass associated with good cohesion and water absorbance. They may not even need the high molar mass to be effective. Increasing the binder dosages increases the pellet silica content thus setting a maximum for the dose as one of the main reasons for studying the organic binders is lowering the silica. Another question is whether the reactions of the common organosilanes are fast enough to take place during the pelletization process. However, there are some possible solutions to solve these problems but the crucial thing is the bond strength of the methallosiloxane.

9. Research materials and methods

9.1. Iron ore

The magnetite concentrate was stored in a drum. Before using the concentrate for testing the moisture and particle size differences possibly formed in the barrel during storage were evened out. The material was divided into 3 kg portions, ensuring that each batch contained homogenous material.

The chemical composition, particle size distribution and zeta potential of the iron ore used for testing the organic binders were examined.

9.1.1. Chemical composition

The chemical composition of the concentrate was analyzed using X-Ray Diffraction (XRD) - crystalline structure analysis and X-Ray Fluoresence spectrometer (XRF). The sample was ground to fine powder and the XRD analysis was conducted using PANalytical X'Pert PRO MPD operating with Co Kα radiation (λ=0.1791 nm). The 2θ scan range was 7-90 ° with a step size of 0.0167 and the total time of the run was 60 minutes.

The XRF analysis was carried out using a PANalytical AXIOS (WD-XRF 2.4 kW, Rh Tube) X-ray fluorescence spectrometer and the scan-based semi-quantitative Omnian application. 0.5 g microwax was added to 5 g of ground sample for binder and the mixture was pressed into a pellet. The calculated parameters for Omnian analyses were no normalization, Fe as Fe3O4, other elements as oxides.

9.1.2. Physical composition

The particle size distribution was measured by laser diffraction analyzer (Malvern Mastersizer 2000SM). A spoonful of concentrate was measured in methanol with stirring of 2500 rpm. Two parallel samples were prepared from the concentrate and both samples were analyzed three times. The refractive index was 2.7 and absorption index was 0.1. The results are for 10%, 50% and 90% volume based percentiles. That is e.g. 10 % of the particles are smaller than the given value in µm.

The zeta pontential of the concentrate was measured using the Malvern Zetasizer Nano – instrument. Two parallel samples were prepared from the concentrate and both samples were analyzed twice at different pHs. To prepare the samples a spoonful of concentrate was

dispersed in 250 ml of 1mM KCl. The zeta potential of the parallel samples were first measured at natural pH and then repeated after adjusting the pH by adding 0.1 M hydrochloric acid (HCl) or 0.1 M kalium hydroxide (KOH).

9.2. Binders

Three different binder groups were selected for further investigation. These include CMC, polymers and silanes. The viscosities and charge densities were measured for all the tested CMC and polymer binders. These values were not tested for the silanes as they are not soluble in water.

Three different types of CMC binders were selected for testing. Two silanes from Wacker were tested for pelletizing, and their chemical structures shown below.

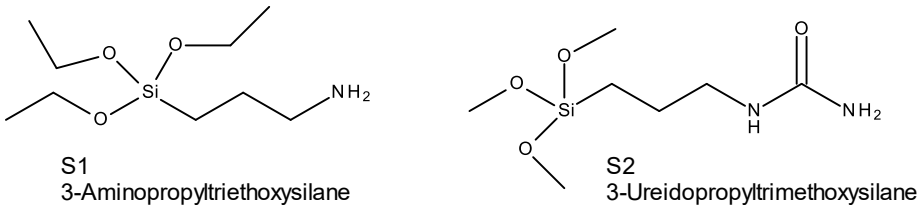


Figure 25. Chemical structures of tested silanes *[27]*.

Polyamides were available with amide groups substituted to carboxyl groups at different degrees. Thus it was possible to test how the presence of an anionic carboxyl group effects the adhesion properties of the binder and consequently the pellet properties. The polyamides, with some the amide groups with an acid group, were assigned binder codes P0, P10, P50 and P90. Polymer binders P1 and P10 have been used commercially for iron ore pellet production and were selected as the reference organic binders. Bentonite was also used as a reference, to compare all the tested binders to a commercial binder currently used in the industry. The different binders and the assigned binder codes are shown in the table below.

Table 13. Assigned binder codes for the tested binders and their type.

Binder	Type
Bentonite	Silica clay
CMC1	CMC
CMC2	CMC
CMC3	CMC
P1	anionic polymer
P0	neutral polyamide
P10	anionic acrylate arylamide copolymer
P50	anionic acrylate arylamide copolymer
P90	anionic acrylate arylamide copolymer
S1	3-Aminopropyltriethoxysilane
S2	3-Ureidopropyltrimethoxysilane

The viscosities and charge densities of polymer and cellulose binders tested for pelletization were measured.

9.2.1. Adjusting the polyamide viscosities

In order to have fewer variables between the different polyamides, the aim was to chop the chains so the polymers would have approximately the same viscosity. Thus the polymers P50 and P90 were modified in order to lower their viscosity to the level of the nearly neutral polymer P0. P10 had been used commercially so it was not chopped, so that it could be used as another reference for a good organic binder.

2.0 w-% solutions were prepared from the powdered P0, P50 and P90 polymers by measuring 490.00 g of water, stirring it vigorously with a mixer and adding 10.00 g of the polymer slowly to the edge of the whirl. Mixing was continued for 3 minutes, then the mixer was set to a low speed and the polymer was left to dissolve up to an hour.

The P50 and P90 solutions were made acidic by adding 5 M HCL. The solutions were then heated at 70 °C for 45 minutes and hydrogen peroxide (H_2O_2) and sodium bisulfide ($NaHSO_3$) was added at a 1:1 molar ratio, while stirring by hand as the solutions were too thick for magnetic stirring. If the solutions had bubbles they were removed on the ultrasonic bath. The viscosities of the solutions were then measured. The P0 solution was used as a reference for the viscosity. The heating of the solutions and the 30 m-% H_2O_2 and $NaHSO_3$ addition (1:3) were repeated until the viscosities were close to the reference. After achieving the level of P0 viscosity, the polymer was precipitated by adding acetone. The solid polymers were ground and sieved through a 250 µm to make sure they were fine enough in order to be evenly mixed with the concentrate for pelletizing.

9.2.2. Viscosity

The viscosities of the binders were measured with using a Broodfield DV-1 viscometer at 25 °C, which was set using a water bath. For the 2.0 % solutions of P50 and P90 were measured using spindle 31, at 3, 6 and 12 RPM. The viscosities of the tested binders, including the modified P50 and P90, were measured for 0.5 w-% solutions with the spindle 18 at 12, 30 and 60 RPM, as they had significantly lower viscosities due to the lower polymer concentrations. The binders with low viscosities did not give reliable results at the lower RPM, whereas the more viscous binders could not be measured with the high RPM. Thus the viscosities were measured at several different revolutions per minute due to the big difference in viscosities between the different binders.

9.2.3. Charge density

For polymers P0, P10, P50 and P50 nominal charges were available. For the other binders the charge densities were measured by performing a polyelectrolyte titration using a Mütek™ PCD-05 particle charge detector. In this method an oppositely charged polyelectrolyte of known charge level was added to the sample as a titrant, neutralizing the charges of the sample. The titration was stopped as soon as the point zero charge was obtained, which could be identified by measuring the streaming potential with the particle charge detector.

The sample solid contents were determined by weighing it before and after drying. The samples were made into 0.04 w-% solutions and placed into the measuring cell one at a time. Poly-diallyldimethylammoniumchloride concentrate was diluted to 0.389 g/l to get the 0.001 N cationic polyelectrolyte titrant. The specific charge density (eq/g) can then be calculated using the following equation:

$$q = \frac{Vc}{m} \tag{3}$$

where V is for consumed titrant volume (l), c is the titrant concentration (eq/l), m is the active substance of the sample, i.e. solid content of the polymer (g).

9.3. Pelletizing

The pellet quality between different batches can vary slightly even if they have the same moisture, which can be difficult to achieve. Thus three batches were produced with each binder and the average of their results were used to compare the performance of binders.

Particles larger than 1 mm were removed and 3 kg of the shifted ore was measured and the amount of binder was calculated from the dry weight of the iron oxide.

Bentonite bound reference pellets where produced with 0.8 w-% of bentonite clay, whereas organic binder bound pellets were produced with 0.05 w-% binder, with organic binder and Na_2CO_3 additive at a 3:1 ratio. All the organic binders were sieved through a 250 µm sieve before weighing. The binder was sprinkled on the concentrate and mixed in by hand and sieved through the sieve. Silane was added together with some of the water with a syringe as it was too thick to spread evenly by itself. After adding the binder, the ore was sieved through the 1 mm sieve again to make sure the binder was distributed evenly within the concentrate. The water, also calculated from the dry weight of the oxide, was sprayed evenly onto the ore aiming for 9.5% moisture, as it decreased to approximately to 9.0% during the process, due to evaporation. The moist ore was then sifted through again to distribute the moisture more evenly and pelletized after 30 minutes.

200 g of the concentrate was placed in to a rotating balling drum with 25 ◦ tilt angle to produce the seed balls. Additional water was sprayed to start the agglomeration, and also during the procedure if the pellets started to look dry. If new seeds were formed the pellets were too dry. The rest of the ore-binder mixture was placed on a conveyor belt which added more ore at a steady 300 g/min rate during 10 minutes. If the pellets became too moist with the added moisture exuded to the surface, the drum was stopped to cover the pellets with more concentrate to decrease the surface moisture. If the pellets became dry, conveyer was stopped to exude more moisture, increasing the pellet surface moisture in order to keep them growing. This caused the pelletizing time to deviate slightly from the 10 minutes for some binders.

9.4. Testing pellets

The pellets were than sifted through a series of sieves to divide the pellets into large (12.7-19 mm), medium (10-12.7 mm) and small (8-10 mm) fractions for the tests. The pellets smaller than 8 mm diameter were discarded after weighing. Drop number and wet strength were measured from the green pellets immediately after weighing the fractions, before the pellets started drying. Rest of the pellets were dried for at least 12 hours at 105 ˚C. The moisture content of the large pellets were measured by weighing them before and after

drying to ensure the moisture was within the 8.85-9.15 %. Some of the medium sized pellets were used to measure the dry strength. Approximately 180 g of pellets from both the dried small and large fractions each and 350 g from the medium fraction were sintered at 1270˚C for 10 min. Some of these pellets were used to determine the strength of sintered pellets and the tumbling index.

The dry strength of the pellets was measured from the medium size fraction before they cooled down as they tend to be stronger when hot. The pellets would not have time to cool down in commercial production and thus measuring them hot gives an idea how the pellets would perform in production conditions.

9.4.1. Drop number

For testing the drop number, 10 of the roundest medium sized (10-12.7 mm) pellets were selected. The test was conducted by dropping the pellet from the standard 45 cm height on to a steel plate until a fracture was observed. The drop number was given by the amount of drops a pellet can take before breaking. The average value of the 10 pellets was reported as the result.

9.4.2. Wet, dry and sintered compressive strengths

The compressive strengths of wet and dry pellets were measured using the Brookfield CT3 Texture Analyzer. The compressive strength tests on sintered pellets were conducted using the Instron 3366. 15-20 successive tests were done on wet, dry and sintered pellets with 10-12.7 mm diameter to determine their compressive strengths.

9.4.3. Porosity and tumbling index

The true density of the pellets were measured using Micrometrics Accupyc II 1340 Gas Pycnometer. The sample chamber was then flooded with helium gas, which fills the pellet pores, to calculate the sample volume. From the weight and volume, the computer program calculated the density. The sample pellets were selected from the 10-12.7 mm and a few smaller pellets were used to get the filling degree of the sample chamber closer to the 80 % required for achieving good results.

The envelop density, the density including the pores, was measured using the Micrometrics GeoPyc 1360 Envelope and T.A.P Density Analyzer. The same pellets that were measured with the Accupyc, were used for determining the envelop density. The samples were weighed again as they may have been abraded when placed in the Accupyc sample container. The

pellets were then carefully placed into a sample chamber filled with fine sand which was packed tightly around the pellets. The instrument than determines total volume of the pellets by comparing the volume of the sand and the sample to the sand volume measured before the sample. From the volume and weight, it then calculated the envelop density. Due to the inaccuracy of the method, the whole procedure was repeated and the average of the two densities is used to calculate the porosity.

The porosity was calculated from the two density values obtained using the different instruments:

$$porosity = \frac{\rho_{true} - \rho_{envelope,Av}}{\rho_{true}}$$

where ρ_{true} is the true density of pellets measured with the Accupyc II 1340 Gas Pycnomete and $\rho_{envelope,Av}$ is the envelope density measured with the, which includes the pores in the volume GeoPyc 1360 Envelope.

The tumbling test was executed according to the standard ISO 3271 *[26]* to determine how abrasive the pellet surfaces were. Approximately 515 g of sintered pellets were weighed before the test and placed into a tumbling drum, which was rotated for 14 minutes due to a smaller drum than in the reference. The pellets and dust were carefully removed from the drum using a brush and sieved to separate the fraction with pellets larger than 6.73 mm, smaller pieces and dust. The fractions were than weighed and the tumbling index was calculated by dividing the weight of pellets after tumbling with the weight before tumbling.

10.Results

10.1. Iron ore

The chemical composition, particle size distribution and zeta potential of the iron ore concentrate used for pelletizations were analysed. The elemental composition analysed by XRF is shown in table 14.

Table 14. The composition of the iron ore.

Element	Mg	Al	Si	P	S	Cl	K	Ca	Cr	Mn	Fe	Na
Conc. %	0.3	0.04	**2.76**	0.01	0.006	0.007	0.01	0.6	0.02	0.10	**62.94**	ND

The X-ray diffractogram is shown in appendix 1. Based on the XRD analysis, the concentrate was found to consist of magnetite Fe_3O_4, Quartz SiO_2, hematite Fe_2O_3 and Calcium Carbonate $CaCO_3$.

The particle size distribution results are presented in the appendix 2 and their averages are shown in the following table. The table 15 indicates the share of particles that are below the given size and the figure 26 shows the particle size distribution.

Table 15. Particle size distribution of the concentrate.

portion of pellet below the size (%)	D(5)	d (10)	d (50)	d (90)	D(95)
particle size (µm)	3.3	4.6	20.1	63.7	83.5

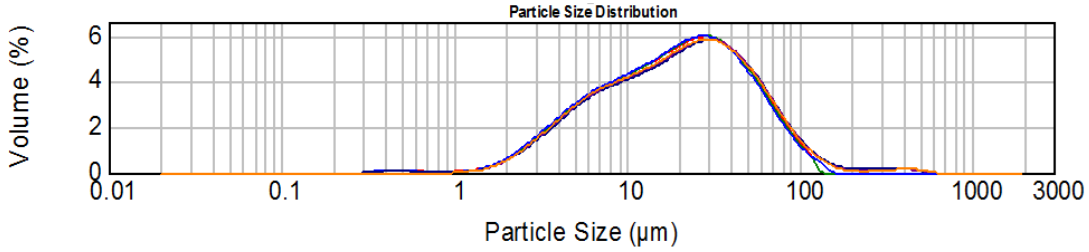


Figure 26. Particle size distribution.

Zeta potential was measured at different pH level and the results are shown in the Figure 27. The graph below shows The zero charge point is approximately at pH 2.5.

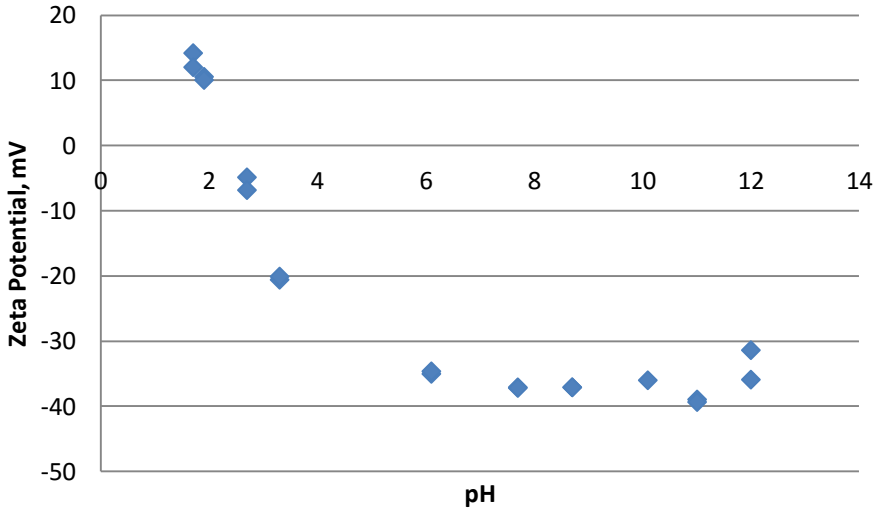


Figure 27. Zeta potential of the iron ore concentrate used for pelletizations.

10.2. Binders

The viscosity of the anionic polymers P50 and P90 were lowered by lowering the pH with HCl, which was not taken into account when aiming for the viscosity of the neutral polymer P0. Thus after precipitating the polymers and dissolving them after grinding them, their viscosities were much higher than expected, approximately three times as viscose as the target viscosity of P0.

The silanes were not water soluble so their viscosities were not measured. The 0.5 w-% binder solutions were mixed for one hour. CMC1 and CMC2 did not dissolve in water entirely. The measured viscosities represent the situation in the pellet moisture.

Table 16 shows the viscosities measured for the different binders as 0.5 w-% solutions.

Table 16. Viscosities and charge densities of polymer and CMC binders.

Sideaine	Varaustiheys (meq/g)	Viskositeetti (cP)
CMC1	1.67	23.6
CMC2	2.29	4.8
CMC3	4.33	7.0
P1	1.65	11.8
P0	0.10	12.5
P10	2.00	53.7
P50	6.10	45.4
P90	10.60	33.3

10.3. Pellets

For some of the more viscose polymer binders, especially P10 and P50, it was impossible to keep the pellets growing while keeping their moisture below 9.15 %. This was because their surface became so dry that new pellets started forming, even when the conveyor was stopped to get more moisture to the surface.

The silanes did not absorb water as they were not dissolved in it. Thus it did not control the growth of pellets and all the moisture was exuded to the surface resulting wet pellets that stuck to each other and even coalesced forming large oval pellets (figure 28). Therefore, silane was tested as an additive with the anionic polymer binder P10. Same amount of polymer was added to the concentrate as with sodium carbonate so that the pellets produced with the different additives could be compared. Adding silica in addition to the

polymer was found to increase the surface moisture of pellets without increasing their moisture content. Thus the conveyor did not need to be stopped to make the surface moist enough to continue the pellet growth and the produced pellets had significantly lower moisture contents than the pellets bound with only P10.

Figure 28. Pellets produced with silane.

The figures of pellets produced with different binders are shown in the following figure.

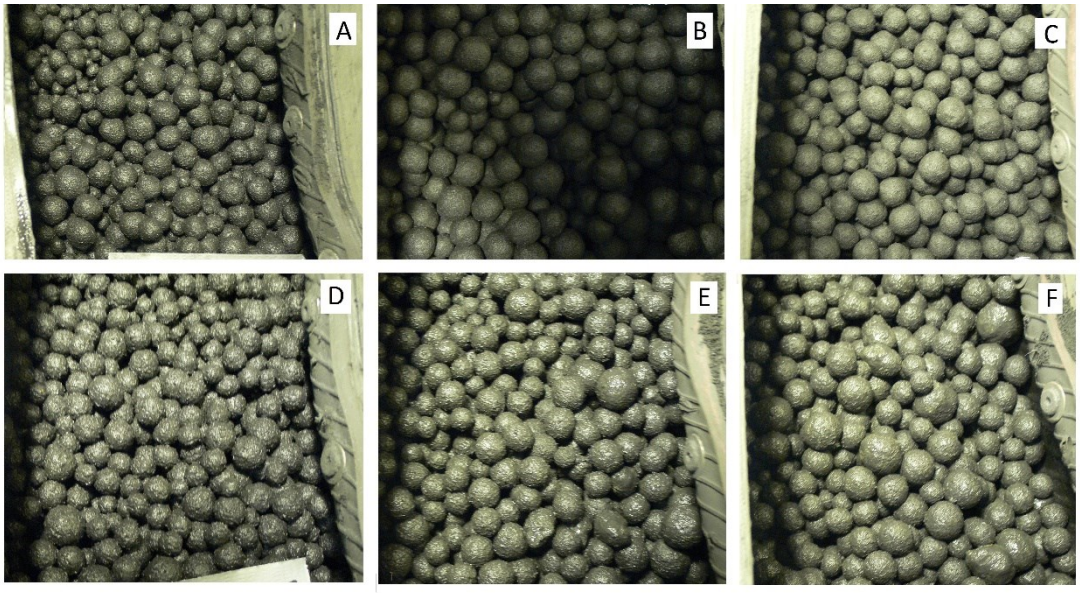


Figure 29. Pellets produced with different binders and the pellet moistures. A: P10 (9.20 %), B: P50 (9.40 %) C: P90 (9.09 %), D: P0, (9.10 %), E: CMC2, (9.21 %) and F: CMC3, (9.17 %).

The surfaces of pellets in the top row of the figure were significantly drier than the ones on the bottom row. Yet the pellet bound with polymer P50, the middle photo in the top row, had the highest moisture contents. This was most likely due to the binders' higher viscosities keeping more of the water within the pellet. Thus it was extremely difficult to produce pellets with low moisture as the surface needed some moisture to keep the pellets growing.

Therefore, if a 9.0 % moisture content is required the binder should have only a moderate viscosity, below 30 cP.

Each binder was tested minimum three times (apart from P0, P10 and bentonite which were tested four times) and the averages of these batches for different pellet properties are given in the tables below (tables 17 and 18). The moistures, drop numbers, compressive strengths, tumbling indices, porosities and size distribution of pellets produced with the different binders are shown. These pellet properties are discussed in more detail in the following chapters.

Table 17. Moisture, drop number, and wet and dry strengths of pellest produced using different binders.

Binder	Moisture (%)	Drop number	Wet strength (g/pellet)		Dry strength (g/pellet)	
			Av.	Std.	Av.	Std.
Bentonite	8.99	3.1	1087	163	3590	403
CMC1	8.96	4.9	1156	159	705	139
CMC2	9.16	2.6	1080	157	1049	168
CMC3	9.16	3.2	1031	175	1513	234
P1	9.04	4.9	881	108	977	148
P0	9.00	3.3	705	98	1055	129
P10	9.23	3.8	862	113	997	154
P50	9.40	2.7	903	95	813	135
P90	9.15	3.0	931	108	689	93
S1 + P10	9.20	5.4	749	107	1020	111
S2 + P10	9.11	4.1	837	120	1211	136

Table 18. Properties of produced using different binders and sintered at 1270 °C for 10 min.

Binder	Sintered strength (kg/pellet)		Tumbling index (%)	Porosity (%)	Size distribution, %			
	Av.	Std.			>12,7 mm	10-12.7 mm	8-10 mm	<8 mm
Bentonite	283.8	54.3	97.4	17.6	13.4	45.7	30.8	10.1
CMC1	265.4	55.7	96.9	17.3	24.1	57.5	13.9	4.5
CMC2	275.9	52.0	96.2	14.3	28.8	52.2	17.2	1.7
CMC3	271.6	45.3	96.3	15.9	17.9	54.3	24.8	3.0
P1	273.3	51.9	97.0	19.8	27.0	59.9	10.5	2.6
P0	231.4	42.7	96.7	19.4	6.4	54.4	32.4	6.8
P10	194.4	42.9	97.3	21.5	2.5	49.3	23.4	17.5
P50	193.0	36.8	97.0	21.7	15.7	60.0	12.5	11.8
P90	198.5	37.1	97.3	19.1	6.3	69.0	17.8	6.9
S1 + P10	195.6	49.9	97.2	19.1	10.7	61.7	18.5	9.0
S2 + P10	182.2	44.9	97.5	21.7	4.4	57.6	25.9	12.1

11.Reviewing results

The aim of this study was to determine the viscosity and charge density a binder should have for it to produce good pellets. The results for polymer and CMC binders were plotted separately in order to see the differences between different binder groups. For most pellet properties it was not very clear what binder qualities produced good results. This was partly due to the order of the viscosities and charge densities being different. Thus if both binder properties had an impact on the pellet properties the graphs would be distorted when drawn for either property alone. Thus only the pellet properties that correlated with the binder properties were plotted and the rest were shown as a bar chart. The charge density and viscosity in some cases had opposite effects for CMC and polymer binders. The results for the CMC however, are less reliable due to less points as only three different binders were tested. In the discussion section one of the aims is to compare the pellets produced with different binders within the binder groups. There were also some issues with the tests as they required craftsmanship and thus the procedure may have varied and improved with practise.

There were also several problems observed with the measurements that effect comparison of the obtained results. These included possible differences in optimal organic binder dosage and pellet moisture content, drying of pellets before drop number tests and abrasion of pellets before tumbling index tests. Comparing the functionality of different organic binders in binding iron ore, when the moisture level and binder dosage may be suboptimal for some while optimal for others, does not give reliable results. The pellet properties and the possible explanations for the differences between pellets produced using the different binders are discussed in the following chapters.

11.1. Pellet size distribution and surface

The 9 % moisture content clearly was not optimal for all binders. Some of the anionic, viscose polymers especially P10 and P50 needed more moisture for the pellets to grow even though the conveyor was stopped for a while to get the moisture to the pellet surface and the final pellet moistures were significantly above 9 %. The produced pellets had very smooth surfaces, however they were not proper spheres as they should be but had sharp corners. The observation of more absorbent binders needing more water in the pelletizing was consistent with the Bureau and Mines study *[12]*. The need to stop the conveyor indicates

the binder might not have worked properly due to too low moisture. Pellet properties could be improved by lowering the binder dosage, or by increasing the moisture content to optimal level.

Some of the CMC binders and the P1 on the other hand produced pellets with very moist surfaces causing them to stick to each other, even though the drum was stopped for short periods in order to keep the pellet growth under control by decreasing the surface moisture. On the contrary to the high viscosity binders, slightly increasing the binder dosage, decreasing the moisture or perhaps adding a small amount of and more absorbing organic component could improve the surface of pellets produced with the low viscosity binders. The smoother and drier surface would make the handling of pellets easier. Thus the pellet moisture content requirements should be considered when selecting the binder.

The growth speed of pellets was estimated by sifting the pellets through a set of sieves and weighing the different fractions. The average size distribution of pellets produced with the different binders tested are shown in the following figure.

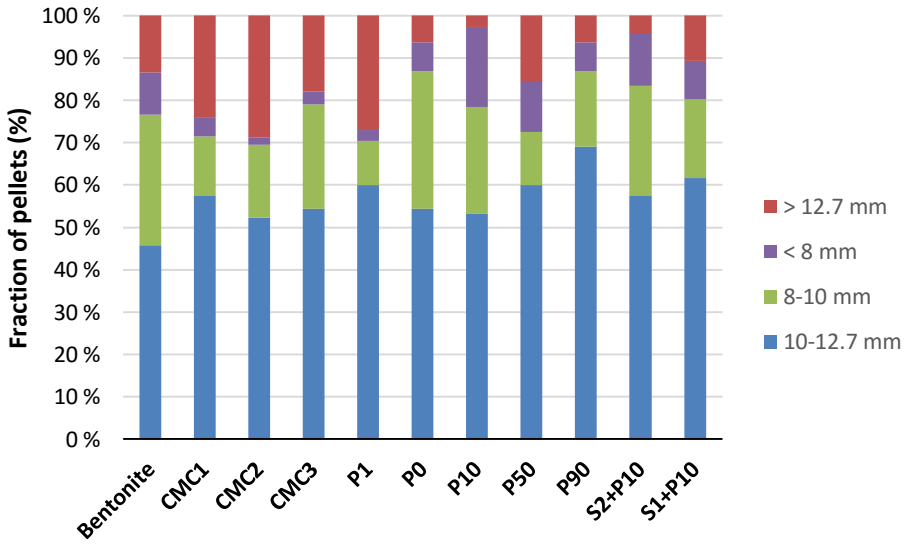


Figure 30. Size distribution of pellets produced with different binders.

Generally 90 % of industrial pellets should have diameter between 10 and 12.7 mm, however this was not achieved for bentonite or any of the other binders *[18]*. However, all the organic binders produced more of the 10-12.7 mm sized pellets than bentonite. However, this may have been due to the fact that bentonite was the first tested binder and the process of pellet production may have improved during the study. The CMC binders and the low viscosity

polymer P1 produced more of the large, over 12.7 mm, pellets than the more viscose polymer binders even though the pellet moisture contents were generally lower. CMC2, the binder with the lowest viscosity, produced nearly no pellets with less than the 8 mm diameter. The size distribution of CMC bound pellets was due to the less viscose pellet moisture which was coalesced to the surface, inducing rapid green ball growth and resulting in larger pellets. P10, which had the highest viscosity of the binders tested, produced the most under 8 mm pellets with even though the batches moisture contents were higher than for most other binders. The high viscosity of the binder prevented it exuding to the surface, resulting in too low surface moisture for the pellets to keep growing. The pellets had to be sprayed with water during the process to introduce the required moisture to the surface, which resulted in very high moisture contents. The addition of silane with P10 increased the surface moisture of the pellets, making it easier to grow them and no additional water was needed after the seeds were formed.

The fractions of pellets with the 10-12.7 mm diameter as the function of binder viscosity were shown in the figure bellow to highlight the effect of binder viscosity on its ability to control the pellet growth.

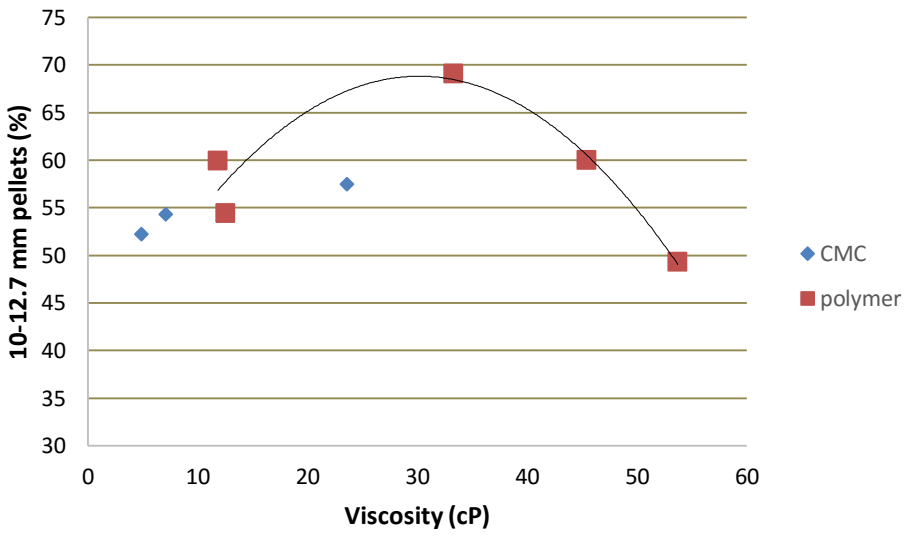


Figure 31. Portion of pellets that have diameter of 10-12.7 mm.

The effect of polymer viscosity on pellet growth and size distribution would seem to follow a second degree polynomic function, with a maximum around 30 cP. A slight increase in fraction of the target sized 10-12.7 mm pellets was observed with the increase of CMC viscosity. CMC binders with viscosity above 30 cP were not tested so it is impossible to say

whether further increasing the viscosity would have a negative effect. The binder needs moderate viscosity, around 30 cP for 0.5 w-% solutions, for it to control pellet growth to produce more medium sized pellets with smooth surface. However, if the viscosity is further increased, it prevents the moisture from getting to the surface, making it too dry for the growth to continue. This differed from conclusions made by *Haas et al.*: "The most effective organic binders for producing pellets with physical properties exceeding the minimum target values had medium PWAT values (>500 and <10,000) in distilled water, high slurry viscosities (>75 cP at 6 % solids), and high adhesive tensile strengths (>4 kg/cm)" *[12]*.

The pellet size distributions of the batches varied greatly even for the same binders depending on the addition rate and amount of water used and whether the conveyor or tyre were stopped in order to control pellet growth. Thus the results for the pellet growth rate might not be reliable. However, there are logical explanations for the results.

11.2. Drop number

Unlike expected, the high viscosity of polymer binders did not seem to improve the wet pellet properties. With CMC binders the drop numbers increased significantly when the binder viscosity was increased (from lowest to highest CMC2, CMC3, CMC1). Same cannot be stated for the polymers as the highest drop numbers were obtained using P1, which had the lowest viscosity of the polymer binders. Both can be seen from the figure below, with the minimum drop number of 5 required by the industry.

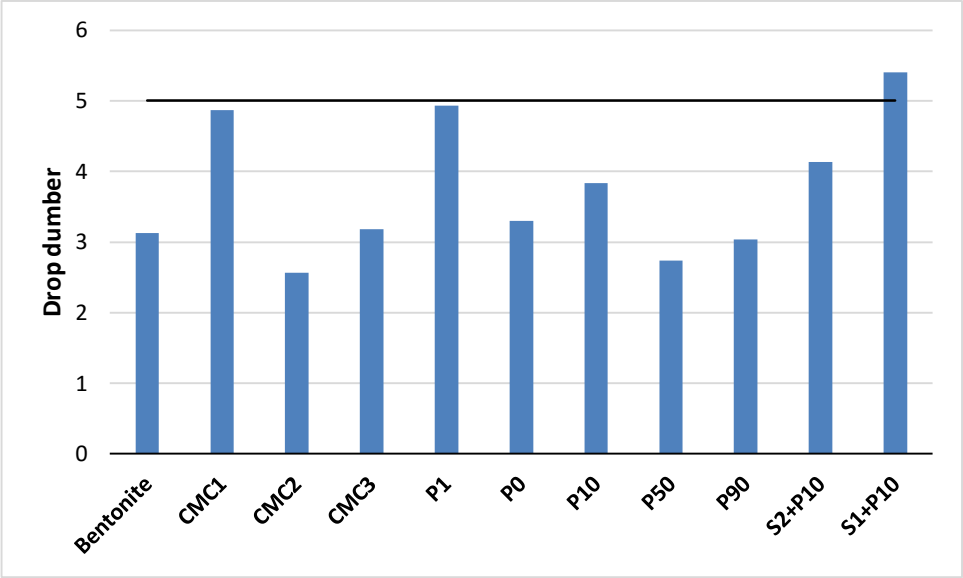


Figure 32. Drop numbers of wet pellets produced with the different binders and the industrially required minimum value drawn as a line.

None of the polymer or CMC binders gave pellets with drop number above 5 but CMC1 and P1 came close with a value of 4.9. Even the commonly used bentonite produced pellets with drop numbers significantly below the required minimum. Only the pellets bound with P10 and aminosilane S1 had the required drop numbers. However, as the pellets had time to start drying before measuring the drop numbers, the values are lower than for the fresh green pellets. This was quite evident from the drop numbers of different batches produced with P10 the result for one of the batches was 8.7 while the average for the other three batches was 3.8. The inconsistent value for P10 was excluded from the results to make it more comparable to the other binders, as it increased the average drop number from 3.8 to 5.1.The moistures and drop numbers for the successful batches with the polymer P10 binder were gathered in the table below to demonstrate the problem with comparing the drop numbers to literature.

Table 19. Moistures and drop numbers for batches produced with P10 polymer binder.

Batch	Moisture (%)	Drop number	Wet strength (g/pellet)
P10-7	9.20	3.60	909
P10-8	9.30	3.30	831
P10-9	9.20	8.70	859
P10-10	9.20	4.60	848

Opposite to what would be expected, the highest drop number was obtained for the pellets with lower moisture content (P10-9). This was due to faster shifting and weighing of the ninth

batch, which means it did not dry as much as the other batches before testing their physical properties. The shifting was slower when low viscosity binders were used as the pellets stuck to each other more giving the pellets more time to dry. Also air moisture may affect the evaporation rate of pellet moisture during the whole process. The drying of pellets before measuring the wet strengths did not seem to affect the results as the strength of P10-9 was closest to the average of the four batches.

The drop number of pellets produced with P10 approximately doubled when done sooner after pelletizing. The difference between the value obtained and the real drop number would most likely be even bigger for pellet bound with low viscosity binders as they took longer to shift and thus had more time to dry. Thus it could be estimated that that the fresh pellets would have had drop numbers approximately double the results. This means all the pellets would most likely have drop numbers above the required minimum value of 5 and the pellets with drop numbers close to five, such as P1 and especially low viscosity CMC1, might have even exceeded the accepted maximum value of 10 drops.

Thus it might be more useful to compare the results to the ones obtained for the bentonite reference binder. Regardless of excluding the deviant drop number for P10, the average was higher than bentonites. CMC3, P0 and P90 produced pellets with drop numbers in the same range as bentonite bound pellets, with the first two slightly exceeding the value of bentonite (3.1). The only organic binders that produced pellets with drop numbers lower than bentonite were CMC 2 and P50. Their values would need to be doubled when fresh to exceed the minimum, as expected especially for CMC2 as it had low viscosity.

Adding silane to the concentrate further increased the drop number of pellets bound with P10 even though the moisture contents of the pellets were significantly lower. This may be due to the increased surface moisture observed during pelletization. The aminosilane (S1) had a more significant effect on the drop number than the ureidosilane (S2), increasing it by half of the original drop number. The difference may be due to the higher moisture content of the pellets.

11.3. Compressive strengths of wet, dry and sintered pellets

Of the organic binders tested, only CMC binders were the only ones to produce pellets with the required wet strength. Though the drying of green pellets affected the pellet drop

numbers, it did not seem to have an impact on their compressive strengths as can be seen from the table 19. The wet strengths of pellets produced using the different tested binders are shown in the figure below, with the industrially required 1 kg/pellet minimum.

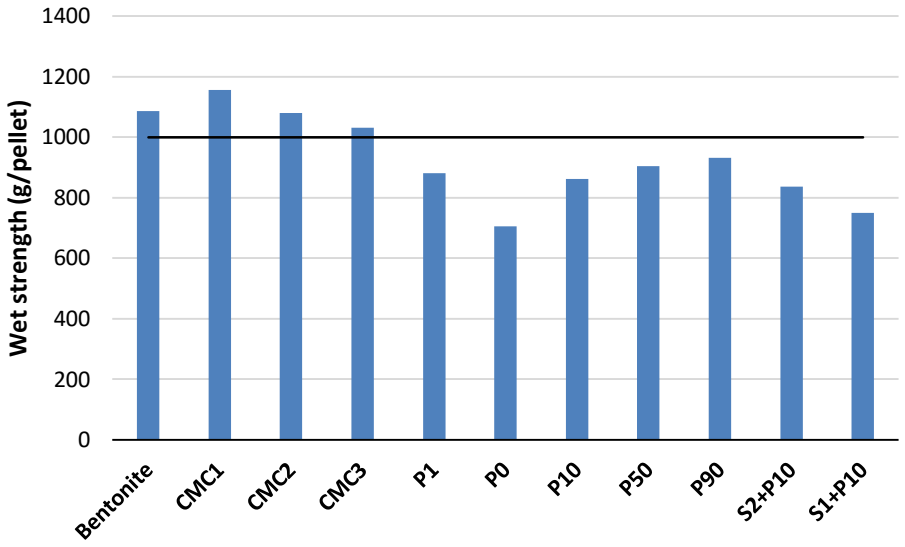


Figure 33. Compressive strengths of wet pellets produced using the different binders and the strength required by the industry as a line.

Pellets bound with CMC1, which had the highest viscosity and lowest charge density of the CMC binders, actually exceeded the compressive strengths of bentonite bound pellets. For CMC binders the charge density had a slight decreasing effect on the strength of wet pellets, whereas the same was not detected for polymer binders. The lowest wet strength was obtained using the nearly neutral binder P0, whereas the rest of the polymer binders gave very similar strengths, with only a slight increase that could be due to variation of results between batches. Therefore, it seemed that a slight charge density of polymer binders helped produce pellets with better wet strength. None of the CMC binders were even close to neutral. Therefore, based on this study, it was impossible to say whether the same applies for CMC binders. Adding the silanes only decreased the wet strengths of P10 bound pellets.

Dry bentonite bound pellets had superior compressive strengths compared to ones produced with organic binders. CMC3 bound pellets, which were the second strongest, were still less than half as strong. As expected from the literature, the dry strength of CMC bound pellets increased with increasing charge density of the binder. However, for the polymers the opposite was observed, with pellet strength decreasing with increased binder charge density.

Both graphs for the compressive strength of dry pellets as a function of binder charge density are shown in the figure below.

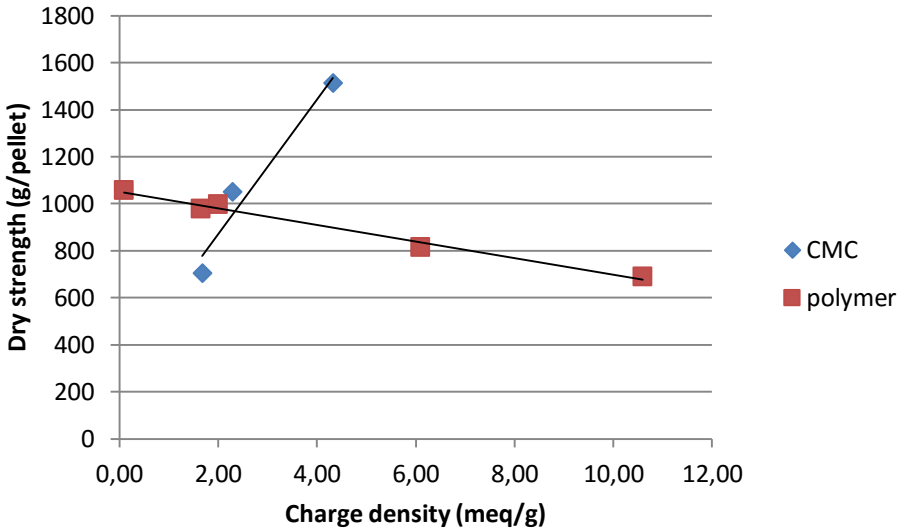


Figure 34. Compressive strengths of dry pellets as a function charge density of the binder.

The linear dependency, despite the different order in increase of viscosity and charge density of binders, indicates that the binder viscosity did not have a significant effect on the dry strength of pellets. Furthermore, binders P1, P10 and CMC2, which had similar charge densities, had very similar dry strengths. The addition of aminosilane S1 seemed to have no effect on the dry strengths of pellets, while ureidosilane increased the strengths of P10 bound pellets from 997 kg/pellet to 1211 kg/pellet.

The CMC bound pellets were again stronger after sintering than the pellets with polymer binders, with no significant difference between the pellets produced with the different CMC binders. The strengths of pellets bound with the different CMC binders were closer to each other than the different batches produced with one binder. Thus the binder properties did not seem to affect the sintered strengths of pellets. The pellet strengths are shown in the figure below with the 250 kg/pellet strength required for industrial production.

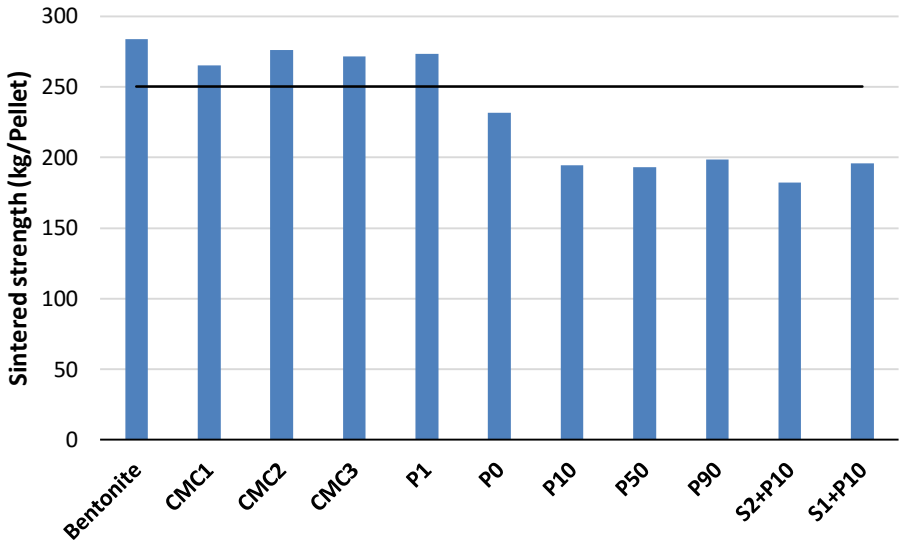


Figure 35. Sintered strengths of pellets and the industrially required strength drawn as a line.

The only polymer binder to achieve pellets with the required strength was the low viscosity and moderate charge density binder P1, with the other low viscosity P0 coming quite close. Thus the polymers with lowest viscosity produced the strongest polymer bound pellets. The values of pellets bound with the more viscose binders were very close to each other, similarly as the CMC bound pellets. The reason for the lower viscosity CMC and P1 binders producing stronger pellets may be their lower porosity. From the more viscose polymers only P90 had a lower porosity than P1. Adding silanes to the P10 bound pellets did not seem to increase the sintered strengths, but the ureidosilane (S2) seemed to even slightly decrease it.

The reason the CMC binders generally produced stronger pellets, apart from the dry strength CMC1, is most likely due to the structure of the modified cellulose. CMC had the optimal functional groups with COO^- as the group interacting with the iron ore and the electron-donating OH to increase the affinity of the anionic group towards the oxide. The structure of P1 is unknown apart from it being an anionic polymer. The rest of the polymers are polyamides with some of the amide groups replaced with anionic COO^- groups. However, while both of the groups have affinity towards the ore, they are electron-withdrawing and may decrease each other's affinity by decreasing the electron density.

11.4. Porosity and tumbling index

The porosities of pellets produced with different binders are shown in the following figure.

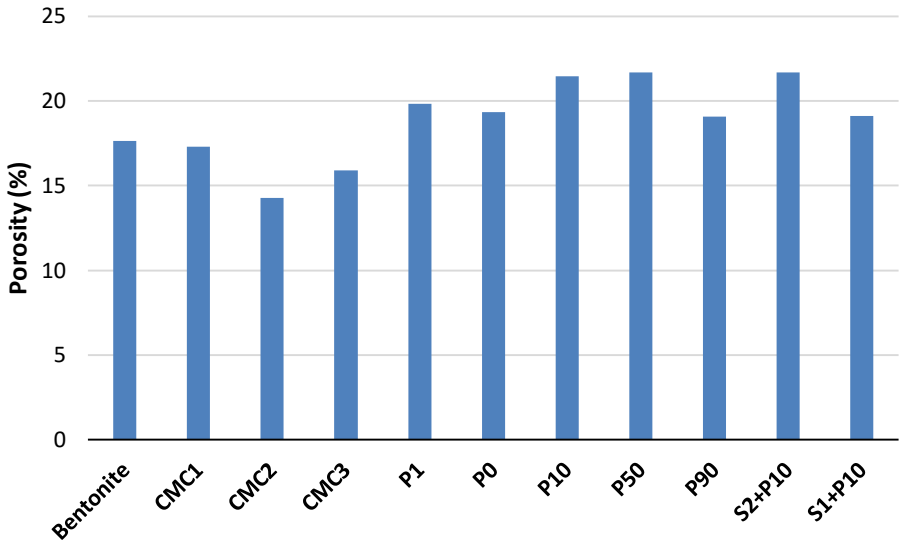


Figure 36. Porosities of pellets produced with different binders.

Unexpectedly, the pellets produced with CMC binders had porosities lower than bentonite, but porosities increased with increasing binder viscosity (from lowest to highest CMC2, CMC3, CMC1) as expected. All the polymer bound pellets had higher porosities than bentonite and the highest porosities were obtained for the two binders with the highest viscosity (P10 and P50). They had the lowest sintered strengths as expected due to the particles having less contact between each other, while all the CMC binders produced pellets with required strengths which was expected due to their low porosities. The effect of porosity on the compressive strengths of sintered pellets can be seen in the following figure.

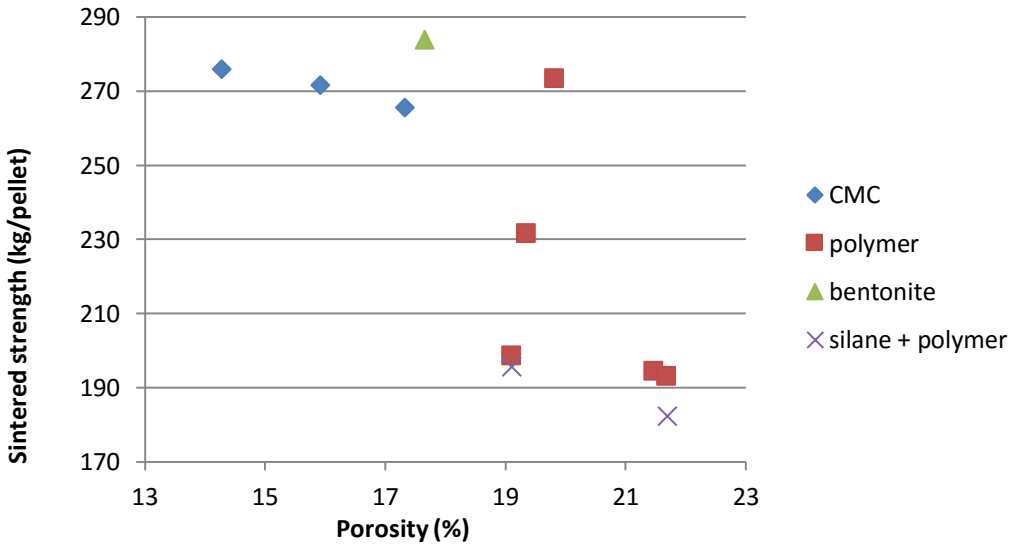


Figure 37. Pellet sintered strengths as a function of their porosities.

On the other hand, the rest of the polymers produced pellets with both the porosities and the sintered strengths decreasing with increasing viscosity. While the high charge density P90, with the optimal viscosity for controlling the pellet growth, produced pellets with the lowest porosity they were some of the weakest. The difference between the porosities however were very small and may be due to the inaccuracy of the method. Adding S1 amino silane decreased the porosity of pellets as expected due to the increased non-combustible material. The pellets bound with the ureidosilane S2 did not seem to have a significant effect on the pellet porosity, which actually slightly higher than with pure P10 polymer binder.

All the tested organically bound pellets had tumbling indices above the required 95 %, with some of them coming close to that of bentonite bound pellets (97.4 %). However, the tumbling index results were questionable as fines were produced already before sintering when the dry pellets were moved from the drying crate for sintering. The pellets with rough surface seemed to produce more fines already during the handling than the ones with smooth surface, which could be seen from the amounts of dust left on the drying and sintering trays. Thus by the time the tumbling tests were done the rough surfaces had already been abraded and thus produced less fines in the drum, which distorted the results. This would mean the indices of the low viscosity binders such as the CMC2, CMC3, P0 and P1, would be slightly lower if the abrading could be prevented before the tumbling. This could be done perhaps by reducing the handling of pellets by drying and sintering them on the same tray and perhaps taking into account the fines produced before the test. All the binders were quite significantly above the minimum, with the lowest result 96.2 %. The 1.2 % difference to the required 95 % corresponds to 6.18 g of dust, which is approximately the amount produced before the tumbling test for 515 g of pellets. Thus all the binders would most likely produce pellets with required resistance to abrasion, even if the procedure was improved so that less dust would be produced before tumbling tests.

The pellets produced with the high viscosity polymer P10 had to be sintered again as the oven did not start lowering the temperature as it was supposed to. The dry pellets had been already bagged for storing which also produced fines before the test but also made them more fragile. Thus during sintering more of them were broken, decreasing the above 6.73 mm fraction.

Regardless of the problems with the method, it could still be observed from the results that high viscosity binders produced pellets with better tumbling index. The polymer bound

pellets generally had higher indices than the pellets bound with the CMC binders, which may have been partly due to their higher viscosities. The effect of binder viscosity on tumbling index is shown in the following figure.

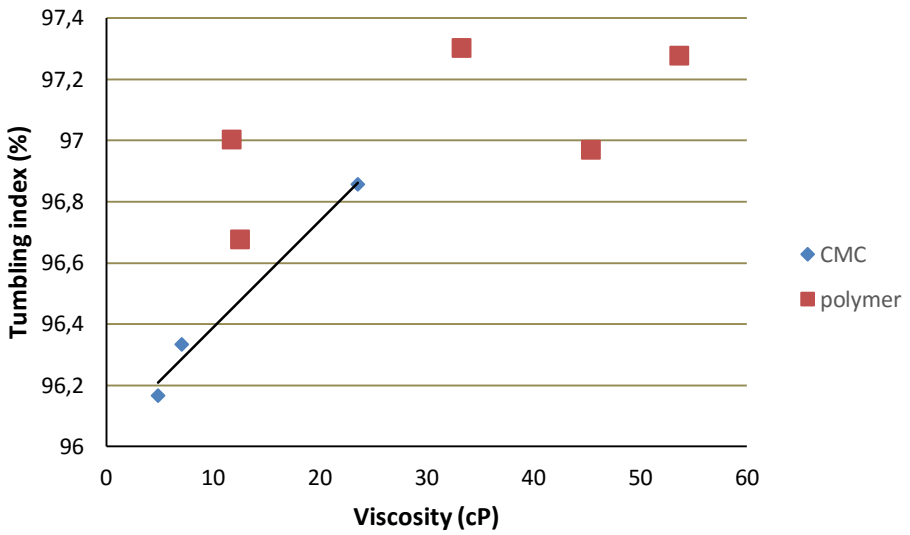


Figure 38. Tumbling index as a function of binder viscosity.

The tumbling index of CMC bound pellets increased with increasing viscosity as expected due to the smoother surfaces. No graph can be fitted to the polymer results in the graph above, but the high viscosity polymers (P10, P50 and P90) produced pellets with higher tumbling index than the binders (P0 and P1). This was due to the smoother surfaces of pellets with more viscose binder. The two binders with lower viscosity would most likely really have even lower indices if the surfaces were not abraded before the tests. Apart from the P0, all the polymer binders produced pellets with higher tumbling indices than the CMC binders. The only CMC bound pellets with higher indices than the low viscosity polymer P0 were the ones bound with the CMC1, which had higher viscosity than the polymer.

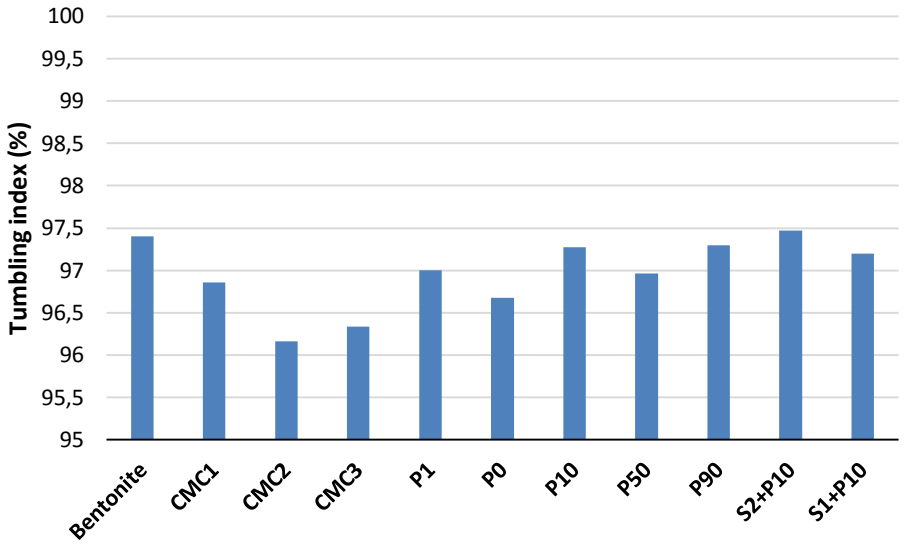


Figure 39. Tumbling indices of pellet bound with different binders. The base line of 95 % is the industrially required minimum.

The tumbling index of pellets bound with P10 polymer binder was improved by addition of ureidosilane S2. The combination was the only one to produce pellets with higher tumbling indices than bentonite. However, the increase was only from 97.3 to 97.5 % and there was more variation between the different batches produced with the same binder than the two averages. On the other hand, both the highest and lowest values between the batches were slightly increased. Nevertheless, the effect was so small it would not be worth adding silane to the concentrate.

11.5. Comparing the CMC and polymer binders

All the tested binders would produce pellets with required abrasion resistance. As expected binders with low viscosity produced pellets with rough, abrasive surfaces, while the highest values were achieved for pellets bound with binders with viscosity above 30 cP. The binders produced pellets with drop numbers of fresh pellets most likely above 5 and ones produced with CMC1 and P1 might even have drop numbers above 10. However, the tests should be redone to be sure. As all the binders would most likely produce pellets with the required tumbling indices and drop numbers, the comparison of results is focused on other pellet properties, mainly their compressive strengths.

According to the results optimal viscosity for binders would be approximately 30 cP at 0.5 w-%, as after this less of the 10-12.7 mm target sized pellets were produced. However, CMC

binders with viscosity that high were not tested. Thus though the fraction of target sized pellets were increased with the increase of CMC viscosity, it is not known whether it starts to decrease when increased above 30 cP.

A slight charge density of polymer binders was found to increase the strengths of wet pellets. On the other hand, the compressive strengths of dry pellets decreased with increasing charge density, which contradicts the findings from literature, and the binder viscosity did not seem to affect the results. While binder viscosity did not seem to affect the dry pellets, it may affect the sintered strengths as the two low viscosity polymer binders produced strongest sintered pellets within the binder group. The ones produced with P1, the slightly charged anionic binder was the only polymer producing pellets with required sintered strength. All the polymer bound pellets were more porous than the bentonite bound pellets. The highest pellet porosities were obtained with the high viscosity polymers P10 and P50 and as expected the produced pellets had the lowest sintered strengths of the polymer bound pellets. Thus according to the observations made in this study, the polymer binders should have moderate viscosities below 30 cP at 0.5 w-% solutions and low charge densities.

Pellets produced with the CMC binders had higher wet and sintered strengths than the polymer bound pellets. They were the only ones to produce green pellets with required compressive strengths. On the contrary to the polymer binders, increasing the charge density increased the strengths of dry pellets and the highest dry strength was obtained with the CMC3, the CMC binder with the highest charge density. The influence of charge density on the wet strength was the opposite, with increasing charge density of binder slightly weakening the pellets. The sintered strengths of pellets produced with the different CMC binders were very close to each other. All the CMC binders produced pellets with lower porosity than the bentonite bound pellets. The lower porosities are due to the low binder viscosities and explain the better sintered strengths of CMC bound pellets compared to the more porous polymer bound pellets.

The reason for the observed differences between the polymers and CMC binders may be due to the difference in their structures. The CMC binders had electron donating hydroxyl groups as the original functional group. Some of them had been turned into COO^- groups, which are considered the optimal functional groups for interacting with the iron oxide surface. The remaining hydroxyl groups donate some of their electron density to the acid groups, increasing their affinity towards the oxide *[11]*. The polymers on the contrary CMC, are

polyamides with some of the amide groups replaced with carboxyl groups – the exception is P1 structure of which is unknown. Thus while both groups have affinity towards the iron ore, they are both electron withdrawing and therefore decrease each other's affinity towards the ore *[11]*. The optimal structure of CMC for binding to iron oxide may also explain the generally higher strengths of pellet when CMC was used as a binder. However, the reasons for the observed effect of the binder properties are not know as the binding mechanism is complicated. More research on different binder structures and testing them for different kinds of iron concentrates could help understanding the trends observed.

The decrease in dry strength with increase of binder charge could have been due to the oxide being charged negatively, not positively like Lee and Somasundaran suggest *[44]*. Thus the adsorption of the binder would be determined by competing hydrogen bonding and repulsive electrostatic interaction, reducing their interaction. However, the same effect was not observed for the other compressive strengths. Furthermore, the strengths of dry pellets bound with CMC binders were found to increase with the binder charge density even though they were also negatively charged.

Both CMC1 and CMC2 were CMC-Na-salts and did not dissolve in water at the 0.5 w-% even after mixing overnight but had different molecular weights. CMC1, with the highest viscosity of the tested CMC binders, had a molecular weight between 400 and 750 kDa. The CMC1 molecules were significantly shorter with molecular weight below 200 kDa and was had the lowest viscosity within the group. CMC1, the higher viscosity binder produces more of the target sized pellets and they had higher drop numbers and wet strength as expected, even though their moisture content was significantly lower. The pellet produced with CMC2 were slightly more porous and thus stronger when dry or sintered. The difference much greater for the dry strengths.

CMC3 was the only CMC that dissolved in water and its viscosity was slightly higher than that of CMC2. As expected, it produced pellets with higher drop strength and porosity than the CMC2. Their sintered strengths were lower, which could be due to the higher porosity, though the difference was rather insignificant. Unexpectedly the dry strengths were significantly better, highest of all the pellets produced with organic binders. This could be due to the CMC3 dissolving in water and thus perhaps interacting better with the concentrate. However, there are also other simple explanations for the high dry strength. It may be partly due to the low porosity of CMC3 bound pellets, although they were more

porous than pellets bound with CMC2. Another factor could be that the CMC3 had the highest charge density of the binder group as it seemed to improve dry strength of CMC bound pellets.

Several of the values for bentonite bound pellets were quite significantly above the required values. Thus the pellets bound with organic binders do not need to exceed the values obtained for bentonite. Hence the values for organic binders were also compared to the required limits for industrial production (table 20).

Table 20. The requirements for different physical properties and the values obtained with the different binders.

Binder	drop number	wet strength (g/pellet)	dry strength (g/pellet)	sintered strength (kg/pellet)	tumbling index (%)
Required values	5-10	1000	2000	250	95
Bentonite	3.1	1087	3590	283.8	97.4
CMC1	4.9	1156	705	265.4	96.9
CMC2	2.6	1080	1049	275.9	96.2
CMC3	3.2	1031	1513	271.6	96.3
P1	4.9	881	977	273.3	97.0
P0	3.3	705	1055	231.4	96.7
P10	3.83	862	997	194.4	97.3
P50	2.7	903	813	193.0	97.0
P90	3.0	931	689	198.5	97.3
S2+P10	4.1	837	1211	182.2	97.5
S1+P10	5.4	749	1020	195.6	97.2

The P1 and CMC binders were the only organic binders tested that produced pellets with the required compressive strengths of wet and sintered pellets. Bentonite was the only binder to produce pellets with the required 2000 g/pellet strength. The highest dry strengths for organically bound pellets were produced using the high charge density CMC3 and were only 1500 g/pellet, which was significantly higher than for pellets bound with any of the other organic binders. Thus the CMC3 would be the best of the binders tested in this study, at least with the dosage and moisture content that were used.

As some of the pellet properties such as the drop numbers and size distribution did not exceed the industrially required values even with bentonite, the values are compared also to the bentonite reference binder. The measured properties of pellets bound with organic binders tested in this study were compared to corresponding values of pellets produced with bentonite by deducting the reference value from the value obtained for pellets produced with the organic binder. Thus negative value indicates the value was below the reference

value obtained for bentonite bound pellets, while positive value indicates value was higher. The remainders are gathered in the following table.

Table 21. Pellet properties compared to ones bound with bentonite. Positive value indicates the value was higher for the organic binder bound pellets than the bentonite bound pellets, while a negative value indicates the bentonite bound pellets had the higher value.

Binder	Moisture (%)	Drop number	Wet strength (g/pellet)	Dry strength (g/pellet)	Sintered strength (kg/pellet)	Tumbling index (%)	Porosity (%)	10-12.7 mm pellets (%)
CMC1	-0.03	1.7	69	-2885	-18.4	-0.5	-0.3	11.8
CMC2	0.17	-0.6	-7	-2541	-7.9	-1.2	-3.4	6.5
CMC3	0.17	0.1	-55	-2077	-12.2	-1.1	-1.7	8.6
P1	0.05	1.8	-206	-2613	-10.5	-0.4	2.2	14.2
P0	0.01	0.2	-382	-2536	-52.3	-0.7	1.7	8.7
P10	0.23	0.7	-225	-2593	-89.4	-0.1	3.8	3.5
P50	0.26	-0.4	-183	-2777	-90.7	-0.4	4.0	14.3
P90	0.16	-0.1	-156	-2901	-85.2	-0.1	1.4	23.3

All of the binders produced weaker dry pellets and sintered strengths than bentonite. Pellets produced with the low viscosity binders such, as CMC and P1, were the only ones to produce pellets with similar sintered strengths as bentonite. The pellet produced with the CMC binders had lower porosity than ones with bentonite.

Adding silanes to the binder increases the silica content of the pellets, which is one of the main reason for substituting the cheap bentonite for organic binders. Thus in order for it to be profitable to add silanes to the binder, the pellet qualities should be significantly improved. The effect of switching the sodium carbonate to silane is shown in the following table.

Table 22. The effect of silane addition with P10 to the pellet properties. Positive value indicates the values of P10 bound pellets were increased with the addition of silane, while a negative value indicates it was decreased.

Binder	Moisture (%)	Drop number	Wet strength (g/pellet)	Dry strength (g/pellet)	Sintered strength (kg/pellet)	Tumbling index (%)	Porosity (%)	10-12.7 mm pellets (%)
S1+P10	-0.03	1.6	-113	23	1.2	-0.1	-2.4	12.4
S2+P10	-0.12	0.3	-25	214	-12.2	0.2	0.2	8.3

Both silanes increased the fraction of 10-12.7 mm pellets produced due to the increased surface moisture due to its hydrophobicity. It may have interfered with the water absorption of the polymer, as smaller amounts of water produced pellets with more moist surfaces and larger fractions of the target sized pellets were produced. In addition to making it easier to control the pellet growth, aminosilane S1 significantly increased only the drop number. The

ureidosilane S2 significantly increased only the compressive strength of dry pellets. Its addition also slightly increased the drop number porosity and tumbling index of pellets, while slightly decreased their sintered strengths. These effects are so minor that they may be due to variation of results. Thus it can be concluded that the tested silanes did not improve the pellet properties enough for them to be viable additives for iron ore palletization.

12. Summary

The aim was to determine what kind of properties of organic binders should have to produce good quality pellets. CMC and polymer binders with different viscosities and charge densities are tested to determine the effects of these properties on the pellet quality. Two silanes are also tested as an additive. The pellet quality is determined by measuring the physical properties of produced pellets: wet drop number and compressive strengths of wet, dry and sintered pellets, as well as porosity and tumbling indices of sintered pellets.

The binder should control the pellet growth to achieve a narrow size distribution so that most of the pellets have 10-12.7 mm diameter. Generally 90 % of industrial pellets would be within the size range, however in this study it was not achieved for any of the binders, including bentonite which had the broadest size distribution in the study. Commonly accepted quality requirements for industrial pellet production include 95 % tumbling index, 1 kg/pellet compressive strength for wet *[18]* and 250 kg/pellet for fired pellets. For the minimum dry pellet strengths acceptable minimum values between 2 2 *[6, 8]* [j, o] and 3 kg/pellet *[18]* have been suggested. The drop numbers of pellets need to be between 5 and 10 for them to have enough elasticity to withstand the handling, but not become plastically deformed. To achieve high tumbling indices, the pellet surfaces should be smooth.

The binder should have good cohesive force between the binder molecules and good adhesive force at the interface between the binder and the ore. Chain interactions and entanglement are increased with increase of molecular weight, which improves both the cohesion and adhesion of the binder. Haas *et al.* suggested binders should viscosities above 75 cP at 6 % solids and PWAT values between 500 and 10,000. However, in this study it was found that after approximately 30 cP for 5 % solutions, increasing the binder viscosity prevents water from exuding to the surface and thus hinder the pellet growth. Thus as

increasing molecular weight increases binder viscosity, there is an upper limit for the length of the binder molecule chain.

To achieve good adhesion, the binder liquid needs to have good wettability towards the iron ore particles, readily spreading on their surface and penetrating between the particles. Thus the binder should reduce the contact angle and reduce the solid/liquid interfacial tension without reducing the surface tension.

Iron oxide concentrates have amphoteric surface sites (M-OH), which can go through either protonation ($M\text{-}OH + H^+ \leftrightarrow M\text{-}OH_2^+$) or deprotonation ($M\text{-}OH + H^+ \leftrightarrow M\text{-}O^- + H^+$) depending on the pH of the moisture. The binder molecule should be adsorbed to these surface sites through functional groups. The functional groups should be polar, such as COOH and $CONH_2$, for them to interact with the charged surface. The organic chain skeleton should have also electron-donating hydrophilic groups such as NH_2 or OH to increase the polar groups affinity towards the ore. The different groups need to be quite close to each other for interaction to be significant *[1]*. In addition to increasing the affinity of the polar group, the hydrophilic group lowers the contact angle between the binding liquid and the iron ore by making it more hydrophilic *[23]*.

While the tested organic binders generally produce good quality green pellets, the pre-heated and sintered pellets tend to lack compressive strengths. This is due to the lack of slag film bonding *[17]*. Optimally the binder skeleton would have double bonds, triple bonds or aromatic or heterocyclic rings to increase the mechanical strength and thermal stability of the binder. This would enable the binder to work longer until the ore particles are sintered together. However, the weakness of pellets bound with organic binders can be compensated by using additives such as sodium carbonate or calcinated colemanite.

Polyacryl amides and CMC, a modified cellulose, have given promising results for pelletizing iron ores. Three CMC binders and four different polyacryl amides were tested for agglomeration and the pellet qualities. Two silanes were tested as additives due to the possible covalent bond formation with the iron ore surface hydroxyl groups.

All the tested binders would produce pellets with required abrasion resistance. As expected binders with low viscosity produced pellets with rough, abrasive surfaces, while the highest values were achieved for pellets bound with binders with viscosity above 30 cP. The binders produced pellets with drop numbers of fresh pellets most likely above 5 and ones produced

with CMC1 and P1 might even have drop numbers above 10. Thus the comparison of results is focused on other pellet properties, mainly their compressive strengths.

The results indicate optimal viscosity for polymers and possibly CMC binders would be approximately 30 cP at 0.5 w-%, which contradicts literature findings. If the viscosity is further increased less of the 10-12.7 mm target sized pellets are produced. However, the CMC binders and the low viscosity polymer P1 were the only ones to produce pellets with required sintered strength. This can be explained with their lower porosities, which results in more contact between ore particles *[32]*. Greater distance may also retard the sintering reactions *[12]*.

A slight polymer charge density produced stronger wet pellets. However compressive strengths of dry pellets were reduced with increasing polymer charge density. The effect was found to be opposite for CMC binders, which could be due to its different functional groups: CMC binder have the optimal functional groups whereas polymers, apart from the reference P1, were polyamides with some of the amide groups changed to carboxylic acids. Thus though both binder types had the carboxyl group with optimal affinity towards iron ore, the CMC binders had electron-donating hydroxyl group to increase the affinity while polyamides had electron-withdrawing amide groups decreasing their affinity.

Pellets produced with the CMC binders had higher wet and sintered strengths than the polymer bound pellets. They were the only ones to produce green pellets with required compressive strengths. This could also be due to its optimal functional groups. CMC3 was found to be the best binder due to its sufficient sintered strength and significantly higher dry strength compared to pellets bound with other organic binders tested.

The silanes increased surface moisture of pellets resulting in larger amount of 10-12.7 mm pellets being produced. In addition to the increased target sized pellet fraction, aminosilane S1 significantly increased only the drop number, while ureidosilane S2 significantly increased only the compressive strength of dry pellets. Thus the silanes tested are not viable additives for iron ore pelletization.

13.Suggestions for further investigation

While verifying the results by testing the binders again would be helpful, it would be more beneficial to compare the binders with their optimal moisture contents and dosages. However, establishing the optimal recipe would require extensive tests and as there are several binders, this would be time consuming. Forsmo *[18]* has proposed that comparing green pellet properties bound with different binders should be done at constant plasticity instead of constant moisture. The plasticity depends on the moisture content of pellets and a certain degree of plasticity refers to the optimum moisture content. The moisture content resulting in 700 µm deformation is considered the optimum, because pellet produced in full-scale balling were found to have the corresponding level of plasticity.

De Moraes, de Limaa and Ferreira Netob *[7]* have proposed a new approach for assessing binder function. They suggested that formation of colloidal wrapping films during the formation of green pellets should be studied. They reported this action to ensure the interstitial viscosity required to pellets stable when wet as well as during and after burning.

Testing the binders with a different iron concentrate would give more information on the interaction between the ore and the binder. Thus the pellets produced from different concentrates using the same binder could be compared. This would give good insight on the effect of oxide surface charge, particle size and chemical composition of the concentrate on the produced pellets. In addition to the test methods used in this study, the zeta potential of the concentrates could be measured with the binder in order to evaluate its suitability for the purpose. If the binders shift the zeta potential of the concentrate to the colloidal stability region, it will cause the oxide particles to repel each other and may retard the palletization. Drying and sintering the pellets would be done on the same tray, less handling would be required resulting in lower abrasion of pellets.

Only three different CMC binders were tested for pelletization. It is rather unreliable to draw graphs with so few measuring points as they can form a straight line by chance. This would then lead into drawing wrong conclusions of the effects of binder properties on the physical properties of produced pellets. Thus more CMC binders with higher viscosities and charge densities should be tested to make sure the trends observed in this study are correct. CMC binders with similar viscosities but very different charge densities, or the other way around, could be also tested to see the effect of the differing variable. This would be important

especially as some of the results are opposite to the ones achieved for the five tested polymers.

Polyacrylic acids could should be tested instead of polyacryl amides as the acid should have higher affinity towards the iron oxide than the amide. Some of the hydroxyl groups should be reduced to hydroxyl groups. The amount of hydroxyl groups or carboxylic groups could be changed to study. Thus the effect of hydroxide substituent on a nearby carboxylic group affinity towards the iron ore and thus its adsorption on it could be investigated.

The best of the tested binders was the CMC3 as it produced pellets with significantly higher dry strengths than any of the other organic binders. However, its low viscosity means the pellet growth is difficult to control and surfaces of green pellets are wet resulting in abrasive rough surface. Thus the binder could be tested together with a superabsorbent that would improve these properties encountered due to its low viscosity.

The organic binder could be tested again by substituting the sodium carbonate to calcined colemanite in order to compare the additive functionalities. As calcined colemanite increases only the sintered strengths the organic binder should produce good property wet and dry pellets *[8]*. None of the pellets produced with organic binders in this study had the required dry strength and the CMC binders were the only organic binder that produced pellets with required dry strength. Their sintered strength was also ab Some of the high viscosity polymer binders could produce good quality green pellets if the binder dosage and moisture content were adjusted. They could also be tested together with calcined colemanite as the additive instead of carbonate.

While the silanes tested in this study did not seem promising, silanes with different structures such as carboxylic functional groups instead of amino or ureido groups could give better results (figure 40). The condensation reaction rate of could also be increased by decreasing the length of the carbon chain between the silicon atom and the organic functional group from the usual propylene to methylene. An electronegative donor as the functional group, such as nitrogen (amine) or oxygen (alcohol or ether), increases this effect activating the alkoxy groups on the silicon when separated only by a methylene bridge. This enhances their

reactivity towards nucleophiles and thus increases the rate of hydrolysis.

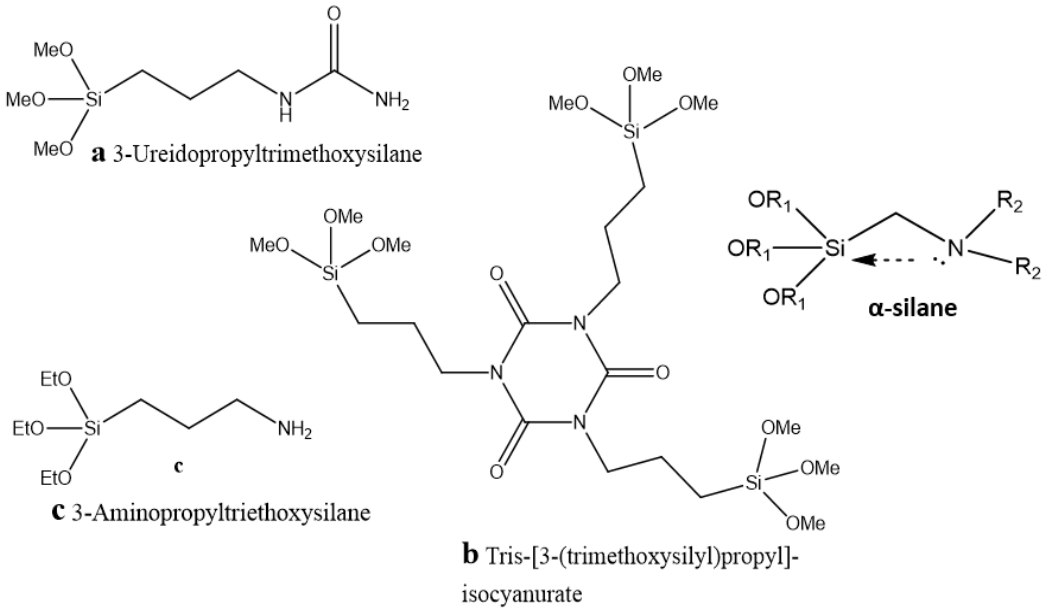


Figure 40. Organofunctional silanes available from Wacker *[27]*.

The silane could be also either attached to a polymer chain by radical crafting or attaching it to a functional group of the polymer (endcapping), or copolymerizated to incorporate the silanol functionality into a polymer *[27]*.

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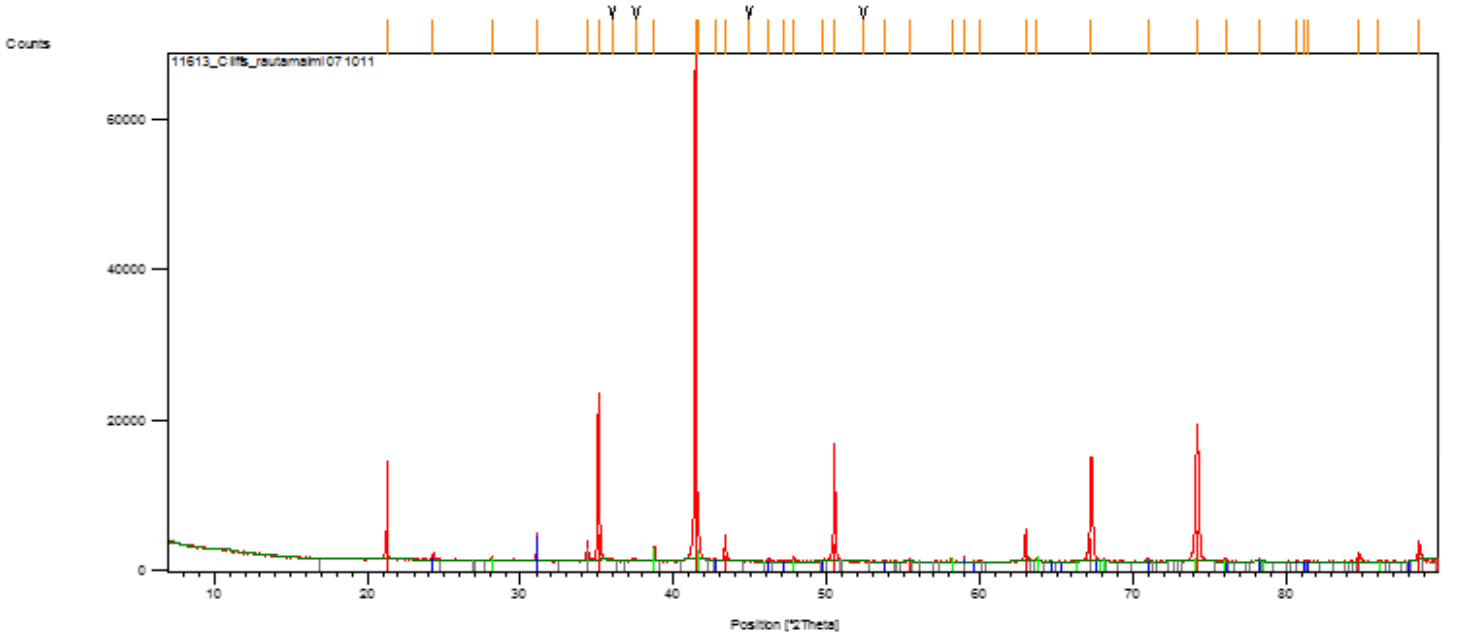
Appendices

Appendix 1: XRD results of the iron ore concentrate.

Appendix 2: Results for particles size distribution and zeta potential measurements.

Appendix 3: Result for zeta potential measurements.

Appendix 1: XRD results of the iron ore concentrate.



Ref. Code	Compound Name	Chemical Formula
01-079-0419	Magnetite	Fe3 O4
01-079-1906	Quartz	Si O2
01-084-0306	Iron Oxide	Fe2 O3
01-070-0095	Calcium Carbonate	Ca C O3

Appendix 2: Results for particles size distribution.

Sample Name	Measurement date and time	D(0.05)	d (0.1)	d (0.5)	d (0.9)	D(0.95)
Cliffs Rautamalmi, 7.10.2011, MeOH, 2500 rpm, 1	12.10.2011 17:24	3.1	4.5	19.5	60.0	76.0
Cliffs Rautamalmi, 7.10.2011, MeOH, 2500 rpm, 1	12.10.2011 17:25	3.1	4.4	19.2	59.1	75.0
Cliffs Rautamalmi, 7.10.2011, MeOH, 2500 rpm, 1	12.10.2011 17:25	3.1	4.4	19.1	59.3	76.2
Cliffs Rautamalmi, 7.10.2011, MeOH, 2500 rpm, 2	12.10.2011 17:35	3.3	4.7	21.1	69.4	94.2
Cliffs Rautamalmi, 7.10.2011, MeOH, 2500 rpm, 2	12.10.2011 17:35	3.5	4.8	20.9	67.5	90.0
Cliffs Rautamalmi, 7.10.2011, MeOH, 2500 rpm, 2	12.10.2011 17:36	3.4	4.8	20.6	67.1	89.6

Appendix 3: Result for zeta potential measurements.

Sample Name	Measurement Date and Time	pH	T	Zeta Potential	Mob	Cond	Attenuator	Note!
			°C	mV	µmcm/Vs	mS/cm		
Cliffs, pH 10,1 1 2	28. lokakuuta 2011 10:50:23	10.1	22	-36.0	-2.669	0.477	8	
Cliffs, pH 11 1 1	28. lokakuuta 2011 10:58:47	11	22	-39.0	-2.888	1.08	7	
Cliffs, pH 11 1 2	28. lokakuuta 2011 11:00:46	11	22	-39.4	-2.918	1.13	7	
Cliffs pH 12 1 1	28. lokakuuta 2011 12:10:11	12	22	-31.4	-2.328	4.5	6	
Cliffs pH 12 1 2	28. lokakuuta 2011 12:12:12	12	22	-35.9	-2.655	5.3	6	
Cliffs, pH 3,3 1	28. lokakuuta 2011 12:36:47	3.3	22	-20.6	-1.523	0.384	6	
Cliffs, pH 3,3 2	28. lokakuuta 2011 12:38:52	3.3	22	-20.1	-1.486	0.386	6	
Cliffs, pH 2,66 1	28. lokakuuta 2011 12:55:47	2.7	22	-4.9	-0.3648	1.45	10	
Cliffs, pH 2,66 2	28. lokakuuta 2011 12:57:45	2.7	22	-6.9	-0.5091	1.51	10	
Cliffs, pH 1,94 1	28. lokakuuta 2011 13:05:58	1.9	22	10.5	0.7779	7.72	6	
Cliffs, pH 1,94 2	28. lokakuuta 2011 13:07:39	1.9	22	10.0	0.7424	7.78	6	
Cliffs, pH 1,7 1	28. lokakuuta 2011 13:14:02	1.7	22	14.2	1.048	13.3	6	
Cliffs, pH 1,7 2	28. lokakuuta 2011 13:15:51	1.7	22	12.0	0.8879	13.7	6	
Clifs, luonnol. pH 6,1 heti liuksen teon jlk. 1	28. lokakuuta 2011 13:40:57	6.1	22	-35.0	-2.592	0.175	8	Luonnollinen pH heti liuoksen vamistuksen jlk.
Clifs, luonnol. pH 6,1 heti liuksen teon jlk. 2	28. lokakuuta 2011 13:43:01	6.1	22	-34.7	-2.57	0.177	8	Luonnollinen pH heti liuoksen vamistuksen jlk.
Cliffs, luonn. pH 7,7 1	28. lokakuuta 2011 13:53:42	7.7	22	-37.1	-2.744	0.181	8	Luonnollinen pH, luos pöydäll mittauksen ajan=>muuttuu, ei säädetty
Cliffs, luonn. pH 7,7 2	28. lokakuuta 2011 13:55:42	7.7	22	-37.2	-2.754	0.185	8	Luonnollinen pH, luos pöydäll mittauksen ajan=>muuttuu, ei säädetty
Cliffs, luonn. pH 8,7 1	28. lokakuuta 2011 15:00:41	8.7	22	-37.1	-2.747	0.226	8	Luonnollinen pH, luos pöydäll mittauksen ajan=>muuttuu, ei säädetty
Cliffs, luonn. pH 8,7 2	28. lokakuuta 2011 15:02:40	8.7	22	-37.1	-2.747	0.228	8	Luonnollinen pH, luos pöydäll mittauksen ajan=>muuttuu, ei säädetty